

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2003-270790

(43)Date of publication of application : 25.09.2003

(51)Int.Cl.

G03F 7/039

C08F232/00

H01L 21/027

(21)Application number : 2002-074306

(71)Applicant : FUJI PHOTO FILM CO LTD

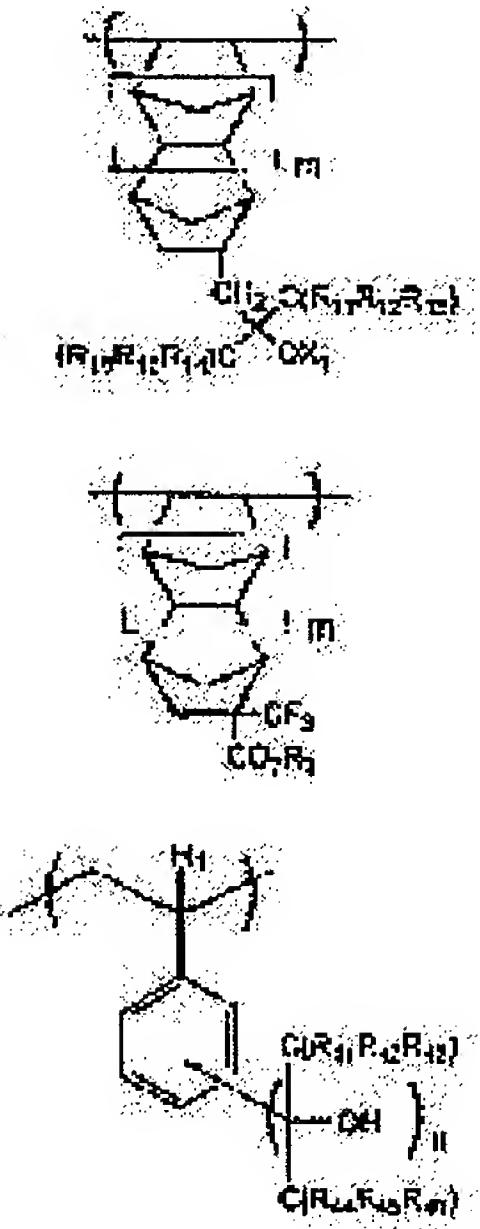
(22)Date of filing : 18.03.2002

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(54) POSITIVE RESIST COMPOSITION



(57)Abstract:

PROBLEM TO BE SOLVED: To provide a positive resist composition having satisfactory transmittance at the time of using an exposure light source of ≤ 160 nm, concretely F2 excimer laser light (157 nm) and improved in line edge roughness and development defects.

SOLUTION: The positive resist composition comprises (A) a compound which generates an acid upon irradiation with an actinic ray or a radiation, (B) an organic fluoropolymer which has at least one repeating structural unit selected from the group of repeating structural units represented by formulae (I)–(II) and a repeating structural unit represented by formula (III) and whose solubility in an alkali developer is increased by the action of an acid and (C) a solvent. In the formula (I), R₁₁–R₁₆ may be the same or different and are each H, F or fluoroalkyl and X₁ is a group which is decomposed by the action of an acid. In the formula (II), R₃ is H or a group which is released by the action of an acid. In the formula (III), R₁ is H, F, Cl, Br, cyano or trifluoromethyl and R₄₁–R₄₆ are each H, F or fluoroalkyl.

LEGAL STATUS

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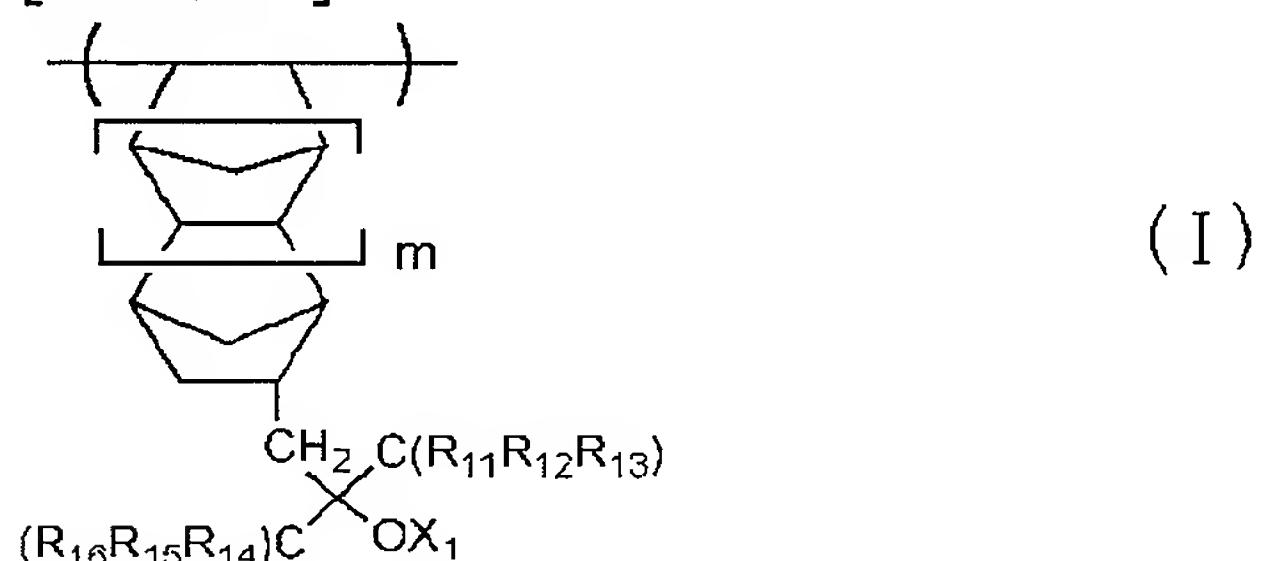
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CLAIMS

[Claim(s)]

[Claim 1] (A) The positive-resist constituent characterized by containing the organic fluorine polymer and the (C) solvent which have the repeat structural unit expressed in the following general formula (III) as at least one sort of the compound which generates an acid, and the repeat structural unit chosen from the group of the repeat structural unit expressed with the (B) following general formula (I) – (II) by the exposure of an activity beam of light or a radiation, and to which the solubility to an alkali developer increases according to an operation of an acid.

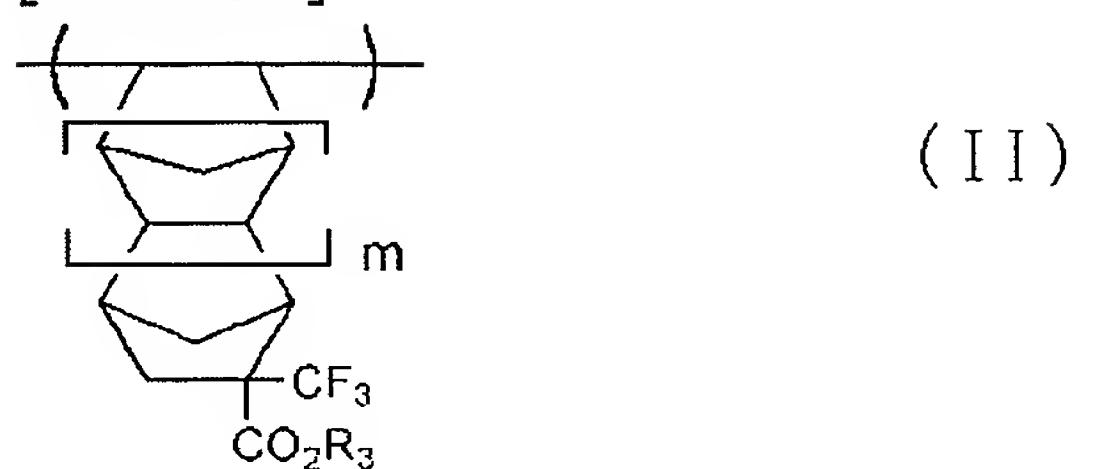
[Formula 1]



In a general formula (I), even if R11–R16 are the same, they may differ from each other, and they express a hydrogen atom, a fluorine atom, or a fluoro alkyl group. However, as for R11–R16, all do not serve as a hydrogen atom. X1 expresses the radical decomposed according to an operation of an acid. m expresses 0 or

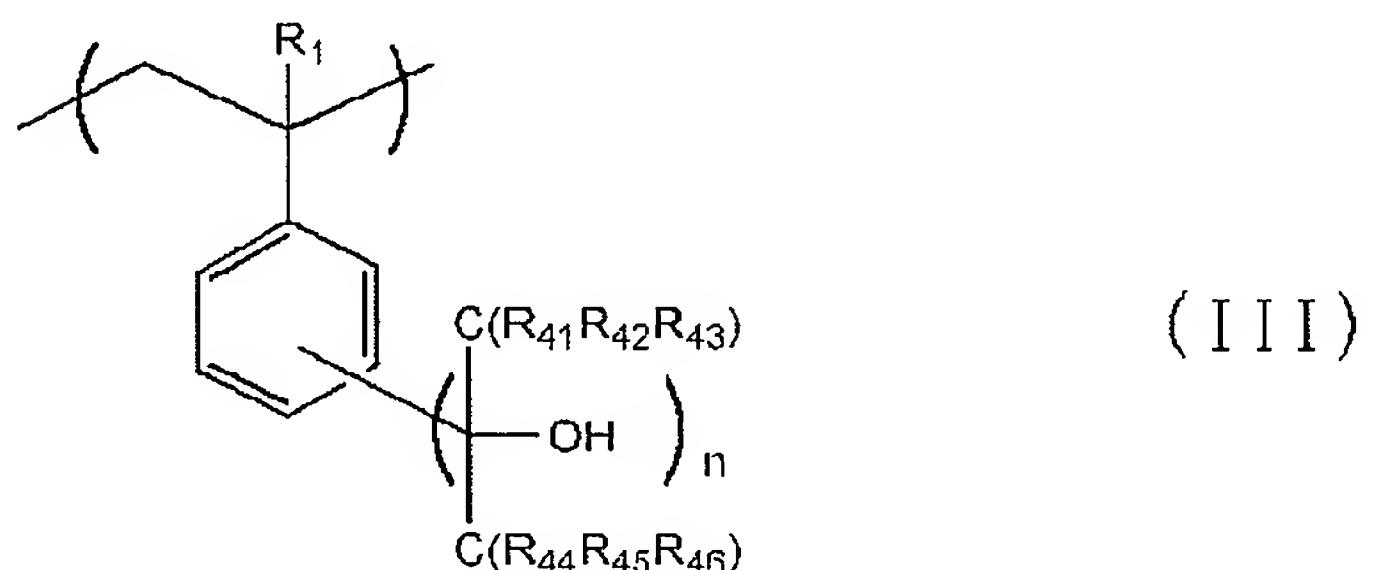
1.

[Formula 2]



In a general formula (II), R3 expresses the radical from which it is desorbed according to an operation of a hydrogen atom or an acid. m expresses 0 or 1.

[Formula 3]



In a general formula (III), R1 expresses a hydrogen atom, a fluorine atom, a chlorine atom, a bromine atom, a cyano group, or a trifluoromethyl radical. even if R41-R46 are the same, they may differ from each other, and they express a hydrogen atom, a fluorine atom, or a fluoro alkyl group. However, as for R41-R46, all do not serve as a hydrogen atom. n expresses the integer of 1-5. when R41-R46 have two or more n or more by two, respectively, even if each R41-R46 which have more than one are the same, they may differ.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the positive-resist constituent used suitable for micro lithography processes, such as manufacture of a VLSI and a high capacity microchip, and other photofabrication processes. Furthermore, it is related with the positive-resist constituent which can form in detail the pattern made highly minute using vacuum ***** 160nm or less.

[0002]

[Description of the Prior Art] the integrated circuit is raising the degree of integration increasingly, and consists of the line breadth below a quarter micron in manufacture of semi-conductor substrates, such as a VLSI, -- processing of a detailed pattern has overly come to be needed. As one of the means which attains detailed-ization of a pattern, short wavelength-ization of the exposure light source used in the case of the pattern formation of a resist is known.

[0003] For example, i line (365nm) of a high pressure mercury vapor lamp has been used for manufacture of the semiconductor device of the degree of integration to 64M bit as the light source to current. As a positive resist corresponding to this light source, many constituents containing the naphthoquinonediazide compound as novolak resin and a sensitization object were developed, and sufficient result has been stored in processing of the line breadth to about 0.3 micrometers. Moreover, instead of i line, KrF excimer laser light (248nm) has been adopted as manufacture of the semiconductor device of a 256 M bit or more degree of integration as the exposure light source. Furthermore, in order to form use of the ArF excimer laser light (193nm) which is the light source of short wavelength, and a pattern 0.1 more micrometers or less from recent years for the purpose of semi-conductor manufacture of the degree of integration beyond 1G bit, use of F2 excimer-laser light (157nm) is considered.

[0004] According to short-wavelengthizing of these light sources, the constituent and its compound structure of a resist ingredient are also changing a lot. The constituent which combined the compound (photo-oxide generating agent) which generates an acid in the exposure of far-ultraviolet light, and the so-called chemistry magnification mold resist have been developed using the resin which made the basic frame small Pori (hydroxystyrene) of absorption in 248nm field as a resist constituent for exposure by KrF excimer laser light, and was protected by the acidolysis radical as a principal component.

[0005] Moreover, the chemistry magnification mold resist which used the acidolysis nature resin which introduced into the principal chain or side chain of a polymer the alicyclic structure which does not have absorption in 193nm as a resist constituent for ArF excimer laser light (193nm) exposure has been developed.

[0006] As opposed to F2 excimer-laser light (157nm) Also in the above-mentioned alicycle mold resin, it becomes clear that absorption of 157nm field is large and inadequate for obtaining the pattern 0.1 micrometers or less made into the purpose. On the other hand, it is reported by Proc.SPIE.Vol.3678.13 page (1999) that the resin which introduced the fluorine atom (perfluoro structure) has sufficient transparency for 157nm. the structure of an effective fluororesin -- Proc.SPIE.Vol.3999.330 page (2000) -- said -- 357 pages (2000) -- said -- it is proposed by 365 pages (2000), WO -00/No. 17712, etc., and examination of the RESHISUTO constituent containing fluorine content resin has been made.

[0007] However, the resist constituent containing the fluororesin for F2 excimer-laser light exposure has problems, such as the Rhine edge roughness and a development defect, and solution of these points was desired. The Rhine edge roughness means originating in the property of a resist and presenting the configuration where the Rhine pattern of a resist and the edge of a substrate interface were irregularly changed in the direction perpendicular to the direction of Rhine. When this pattern is observed from right above, an edge is visible to unevenness (**several nm – about dozens of nm). When this unevenness has large unevenness, it causes a poor electrical property and makes the yield fall, since a substrate imprints according to an etching process.

[0008]

[Problem(s) to be Solved by the Invention] Therefore, the purpose of this invention is offering 160nm or less and the especially suitable positive-resist constituent for use of the exposure light source of F2 excimer-laser light (157nm), and is permeability sufficient at the time of 157nm light source use specifically being shown, and offering a positive-resist constituent with small Rhine edge roughness and development

defect.

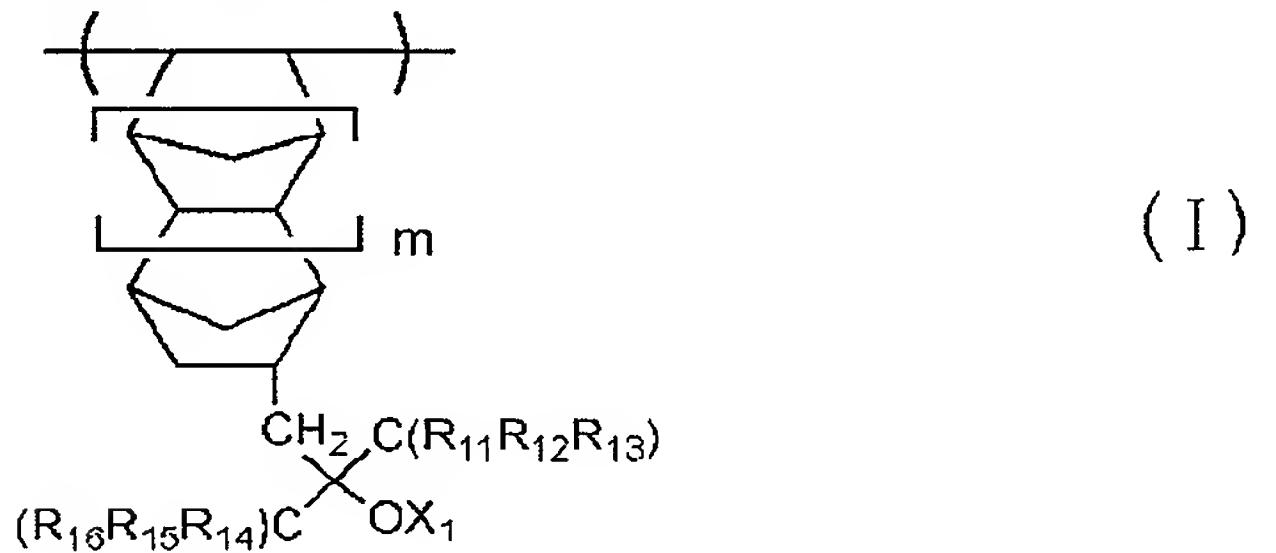
[0009]

[Means for Solving the Problem] this invention person etc. reached [that the purpose of this invention is attained with the following specific constituents, and] a header and this invention, as a result of inquiring wholeheartedly with careful attention to many above-mentioned properties. That is, this invention is the following configuration.

[0010] (1) The positive-resist constituent characterized by to contain the organic fluorine polymer and the (C) solvent which have the repeat structural unit expressed in the following general formula (III) as at least one sort of the compound which generates an acid, and the repeat structural unit chosen from the group of the repeat structural unit expressed with the (B) following general formula (I) – (II) by the exposure of (A) activity beam of light or a radiation, and to which the solubility to an alkali developer increases according to an operation of an acid.

[0011]

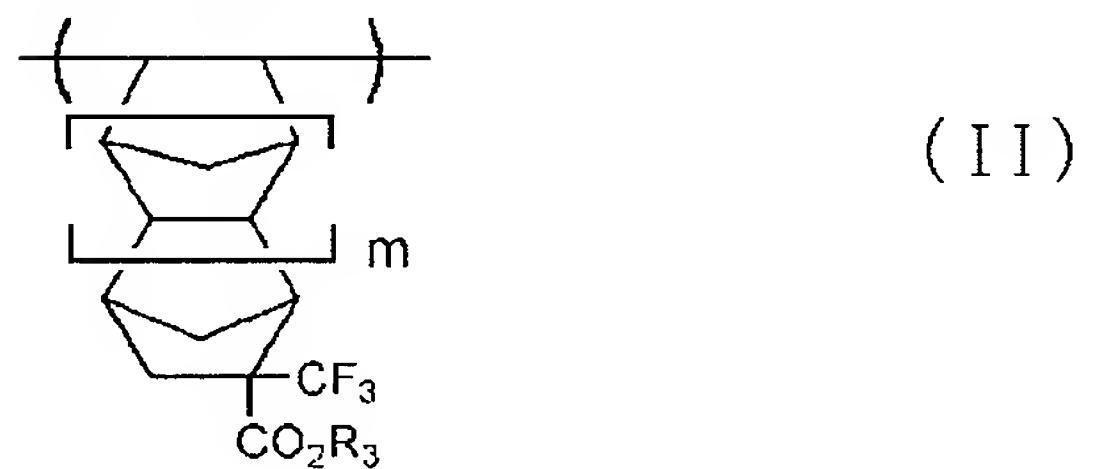
[Formula 4]



[0012] in a general formula (I), even if R11–R16 are the same, they may differ from each other, and they express a hydrogen atom, a fluorine atom, or a fluoro alkyl group. However, as for R11–R16, all do not serve as a hydrogen atom. X1 expresses the radical decomposed according to an operation of an acid. m expresses 0 or 1.

[0013]

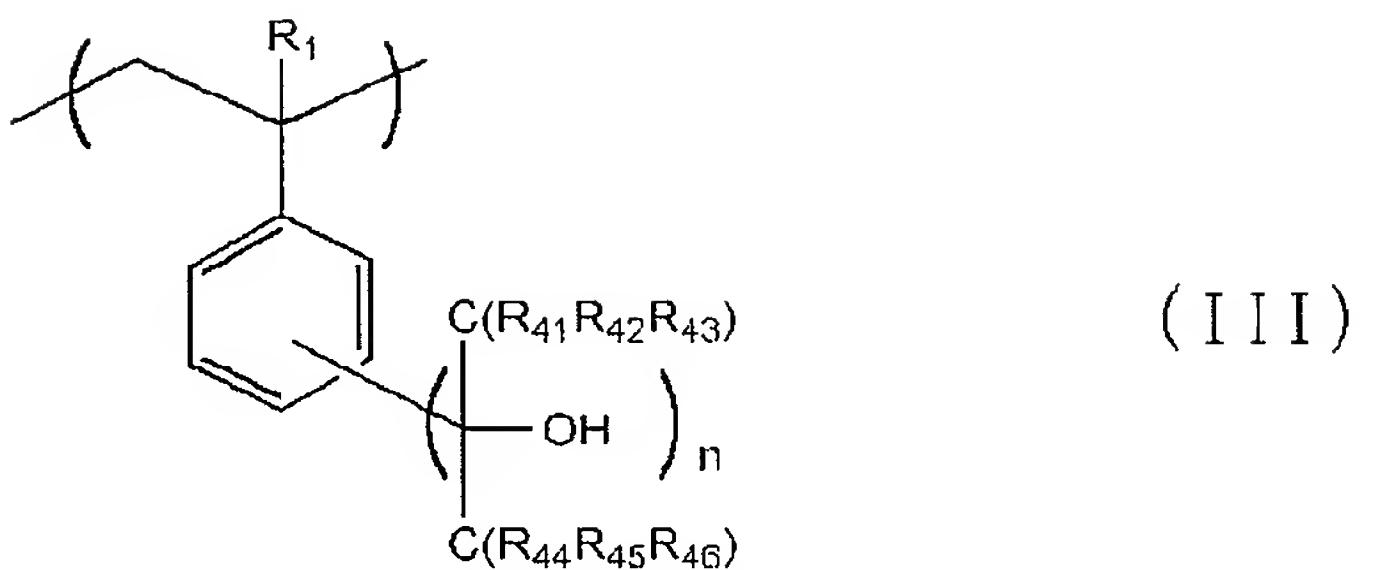
[Formula 5]



[0014] In a general formula (II), R3 expresses the radical from which it is desorbed according to an operation of a hydrogen atom or an acid. m expresses 0 or 1.

[0015]

[Formula 6]



[0016] In a general formula (III), R1 expresses a hydrogen atom, a fluorine atom, a chlorine atom, a bromine atom, a cyano group, or a trifluoromethyl radical. even if R41–R46 are the same, they may differ from each other, and they express a hydrogen atom, a fluorine atom, or a fluoro alkyl group. However, as for R41–R46, all do not serve as a hydrogen atom. n expresses the integer of 1–5. when R41–R46 have two or more n or more by two, respectively, even if each R41–R46 which have more than one are the same, they may differ.

[0017] Hereafter, the mode of desirable operation of this invention is mentioned further.

The organic fluorine polymer of the (B) component further (2) Acrylonitrile (meta), A maleic anhydride, maleimide, N-hydroxy maleimide, N -(t-butoxycarbonyloxy)- Maleimide and C(R1a) (R2a) =C (among a formula) (R3a) (R4a) a positive-resist constituent given in (1) characterized by R1 a–R4a having the repeat structural unit formed of the monomer chosen out of expressing the alkyl group which may differ even if the same, and may be permuted by the hydrogen atom, the halogen atom, or the halogen atom.

[0018] (3) (1) to which R3 in the general formula (II) of the organic fluorine polymer of the (B) component is characterized by being the 3rd class alkyl group, or a positive-resist constituent given in (2).

[0019] (4) A positive-resist constituent given in (3) to which the 3rd class alkyl group is characterized by having an alicyclic ring.

[0020] (5) A positive-resist constituent given in either of (1) – (4) characterized by for weight average molecular weight being [for the organic fluorine polymer of the (B) component] 3000–30000, and molecular weight degrees of dispersion being 1.1–1.5.

[0021] (6) A positive-resist constituent given in either of (1) – (5) to which the organic fluorine polymer of the (B) component is characterized by being obtained by the radical polymerization method.

[0022] (7) A positive-resist constituent given in (6) characterized by being the dropping polymerization method for adding a monomer continuously or intermittently further in case a radical polymerization method carries out the radical polymerization of the monomer under existence of a radical polymerization initiator.

[0023] (8) A positive-resist constituent given in either of (6) – (7) to which the organic fluorine polymer of the (B) component is characterized by pass actuation of removing a component with low molecular weight from the polymer obtained by the radical polymerization method.

[0024] (9) A positive-resist constituent given in either of (1) – (5) to which the organic fluorine polymer of the (B) component is characterized by being obtained by the living polymerization method.

[0025] (10) A positive-resist constituent given in either of (1) – (9) characterized by containing the compound which generates an organic sulfonic acid by the exposure of an activity (A1) beam of light or a radiation as a compound which generates an acid by the exposure of (A) activity beam of light or a radiation.

[0026] (11) A positive-resist constituent given in (10) further characterized by containing the compound

which generates a carboxylic acid by the exposure of an activity (A2) beam of light or a radiation as a compound which generates an acid by the exposure of (A) activity beam of light or a radiation.

[0027] (12) A positive-resist constituent given in either of (1) – (11) characterized by containing propylene glycol monoalkyl ether acetate, and propylene glycol monoalkyl ether or lactic-acid alkyls as a (C) solvent.

[0028]

[Embodiment of the Invention] Hereafter, the compound used for this invention is explained to a detail.

[1] (B) At least one sort of the repeat structural unit chosen from the group of the repeat structural unit expressed with said general formula (I) – (II), The positive-resist constituent of organic fluorine polymer this invention to which the solubility to an alkali developer increases according to an operation of an acid which has the repeat structural unit expressed with said general formula (III) At least one sort of the repeat structural unit chosen from the group of the repeat structural unit expressed with said general formula (I) – (II), The organic fluorine polymer (henceforth "(B) resin of a component") which has the repeat structural unit expressed with said general formula (III) and to which the solubility to an alkali developer increases according to an operation of an acid is contained.

[0029] in a general formula (I), even if R11–R16 are the same, they may differ from each other, and they express a hydrogen atom, a fluorine atom, or a fluoro alkyl group. However, as for R11–R16, all do not serve as a hydrogen atom. X1 expresses the radical decomposed according to an operation of an acid. m expresses 0 or 1.

[0030] The fluoro alkyl group of R11–R16 means the alkyl group by which at least one hydrogen atom was fluoro-ized, its thing of 1–6 carbon numbers is desirable, and the thing of 1–3 carbon numbers is still more desirable. As an example of a fluoro alkyl group, a trifluoromethyl radical, difluoromethyl group, a fluoro methyl group, a pentafluoro ethyl group, 2 and 2, 2-trifluoroethyl radical, 2-fluoro ethyl group, 3 and 3, 3-trifluoro propyl group, 3-fluoropropyl radical, etc. can be mentioned, for example. Especially a desirable thing is a trifluoromethyl radical.

[0031] As a radical (henceforth an acidolysis nature machine) decomposed according to an operation of the acid of X1 For example, –C (R36) (R37) (R38), –C (R36) (R37) (OR39), – COO–C (R36) (R37) (R38), –C (R01) (R02) (OR39), –C(R01) (R02) COO–C (R36) (R37) (R38), etc. are mentioned. R36–R39 express respectively the aryl group which may have the aralkyl radical or substituent which may have the alkyl group which may have the substituent, the cycloalkyl radical which may have the substituent, the alkenyl radical which may have the substituent, and the substituent independently. It may join together mutually and R36 and R39 may form a ring. R01 and R02 express respectively the aryl group which may have the aralkyl radical or substituent which may have a hydrogen atom, the alkyl group which may have the substituent, the cycloalkyl radical which may have the substituent, the alkenyl radical which may have the substituent, and the substituent independently.

[0032] As an alkyl group of R36–R39, and R01 and R02, the alkyl group of 1–8 carbon numbers is desirable, for example, can mention a methyl group, an ethyl group, a propyl group, n-butyl, sec-butyl, a hexyl group, a 2-ethylhexyl radical, an octyl radical, etc. A monocycle mold may be used and it is easy to be in a polycyclic mold as R36–R39, and a cycloalkyl radical of R01 and R02. As a monocycle mold, the cycloalkyl radical of 3–8 carbon numbers is desirable, for example, can mention a cyclo propyl group, a cyclopentylic group, a cyclohexyl radical, cyclo butyl, a cyclo octyl radical, etc. As a polycyclic mold, the cycloalkyl radical of 6–20

carbon numbers is desirable, for example, can mention an adamantyl radical, a norbornyl radical, an isoboronyl radical, a camphor nil radical, a JISHIKURO pentyl radical, alpha-PINERU radical, a tricyclo deca nil radical, the TETOSHI clo dodecyl, a loss TANIRU radical, etc. In addition, some carbon atoms in a cycloalkyl radical may be permuted by hetero atoms, such as an oxygen atom. As an aryl group of R36-R39, and R01 and R02, the aryl group of 6-10 carbon numbers is desirable, for example, can mention a phenyl group, a tolyl group, a dimethylphenyl radical, 2 and 4, 6-trimethyl phenyl radical, a naphthyl group, an anthryl radical, 9, 10-dimethoxy anthryl radical, etc. As R36-R39, and an aralkyl radical of R01 and R02, the aralkyl radical of carbon numbers 7-12 is desirable, for example, can mention benzyl, a phenethyl radical, a naphthyl methyl group, etc. As R36-R39, and an alkenyl radical of R01 and R02, the alkenyl radical of 2-8 carbon numbers is desirable, for example, can mention a vinyl group, an allyl group, a butenyl group, a cyclohexenyl group, etc. As a substituent which R36-R39, and R01 and R02 may have, an alkyl group, a cycloalkyl radical, an aryl group, the amino group, an amide group, an ureido radical, a urethane group, a hydroxy group, a carboxy group, a halogen atom, an alkoxy group, a thioether radical, an acyl group, an acyloxy radical, an alkoxy carbonyl group, a cyano group, a nitro group, etc. can be mentioned.

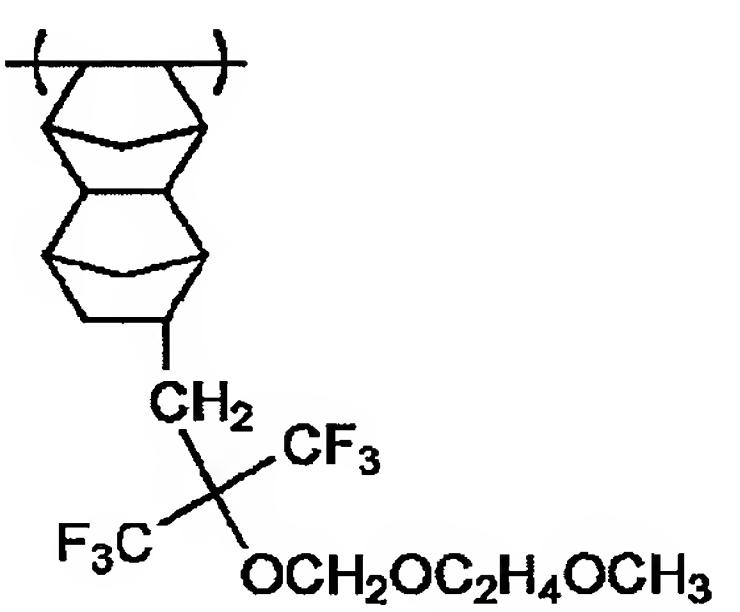
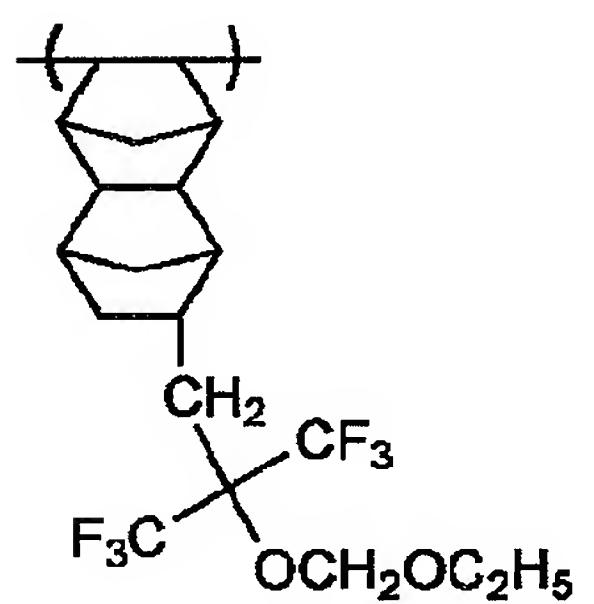
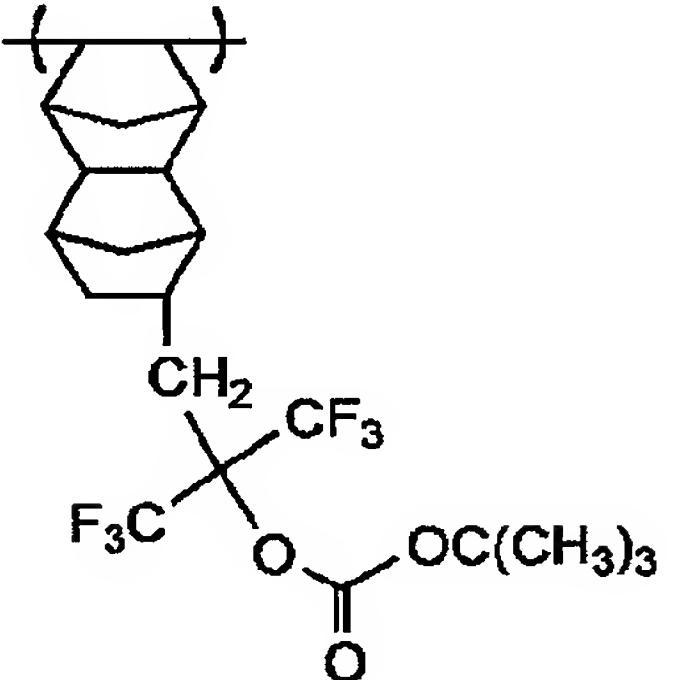
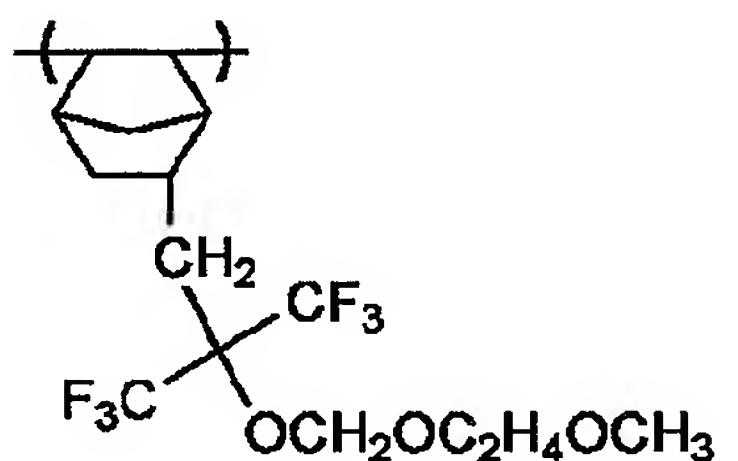
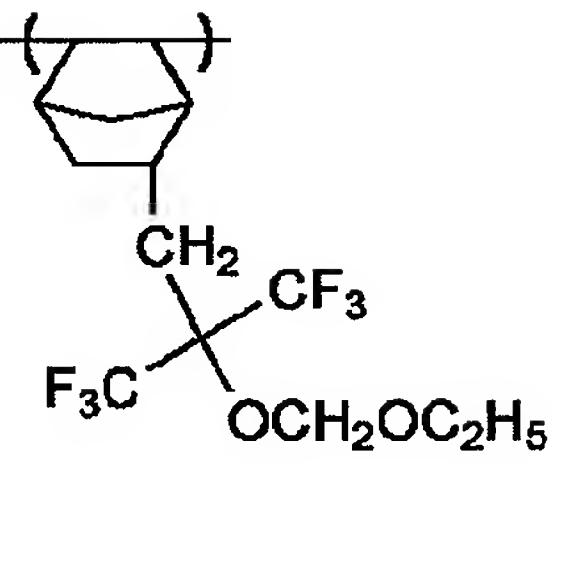
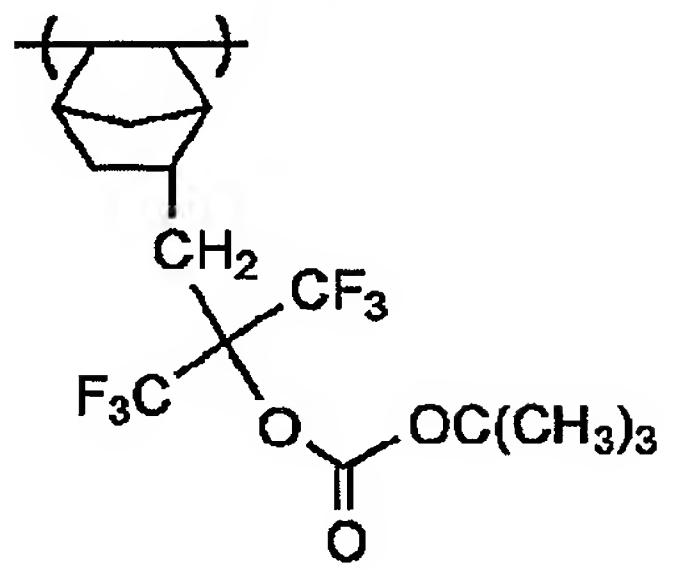
[0033] As a desirable example of an acidolysis nature machine, t-butyl, t-amyl group, A 1-alkyl-1-cyclohexyl radical, a 2-alkyl-2-adamanthyl radical, The 3rd class alkyl groups, such as a 2-adamanthyl-2-propyl group and a 2-(4-methylcyclohexyl)-2-propyl group, Acetal radicals, such as a 1-alkoxy-1-ethoxy radical, a 1-alkoxy-1-methoxy group, and a tetrahydropyranyl group, t-alkyloxy carbonyl group, an ethoxy methyl group, a methoxyethoxymethyl radical, t-alkyl carbonylmethyl radical, etc. are mentioned preferably.

[0034] Although the desirable example of the repeat unit expressed with a general formula (I) is given hereafter, this invention is not limited to this.

[0035]

[Formula 7]

(I) の具体例



[0036] In a general formula (II), R3 expresses the radical from which it is desorbed according to an operation of a hydrogen atom or an acid. m expresses 0 or 1.

[0037] As a radical from which it is desorbed according to an operation of the acid of R3, -C (R36) (R37) (R38), -C (R36) (R37) (OR39), etc. are mentioned, for example. R36-R39 express respectively the aryl group which may have the aralkyl radical or substituent which may have the alkyl group which may have the substituent, the cycloalkyl radical which may have the substituent, the alkenyl radical which may have the substituent, and the substituent independently. It may join together mutually and R36 and R39 may form a ring.

[0038] As an alkyl group of R36-R39, the alkyl group of 1-8 carbon numbers is desirable, for example, can mention a methyl group, an ethyl group, a propyl group, n-butyl, sec-butyl, a hexyl group, a 2-ethylhexyl radical, an octyl radical, etc. A monocycle mold may be used and it is easy to be in a polycyclic mold as a cycloalkyl radical of R36-R39. As a monocycle mold, the cycloalkyl radical of 3-8 carbon numbers is desirable, for example, can mention a cyclo propyl group, a cyclopentyl group, a cyclohexyl radical, cyclo butyl, a cyclo octyl radical, etc. As a polycyclic mold, the cycloalkyl radical of 6-20 carbon numbers is desirable, for example, can mention an adamantyl radical, a norbornyl radical, an isoboronyl radical, a camphor nil radical, a JISHIKURO pentyl radical, alpha-PINERU radical, a tricyclo deca nil radical, the

TETOSHI clo dodecyl, a loss TANIRU radical, etc. In addition, some carbon atoms in a cycloalkyl radical may be permuted by hetero atoms, such as an oxygen atom. As an aryl group of R36–R39, the aryl group of 6–10 carbon numbers is desirable, for example, can mention a phenyl group, a tolyl group, a dimethylphenyl radical, 2 and 4, 6-trimethyl phenyl radical, a naphthyl group, an anthryl radical, 9, 10-dimethoxy anthryl radical, etc. As an aralkyl radical of R36–R39, the aralkyl radical of carbon numbers 7–12 is desirable, for example, can mention benzyl, a phenethyl radical, a naphthyl methyl group, etc. As an alkenyl radical of R36–R39, the alkenyl radical of 2–8 carbon numbers is desirable, for example, can mention a vinyl group, an allyl group, a butenyl group, a cyclohexenyl group, etc. As a substituent which R36–R39 may have, an alkyl group, a cycloalkyl radical, an aryl group, the amino group, an amide group, an ureido radical, a urethane group, a hydroxy group, a carboxy group, a halogen atom, an alkoxy group, a thioether radical, an acyl group, an acyloxy radical, an alkoxy carbonyl group, a cyano group, a nitro group, etc. can be mentioned.

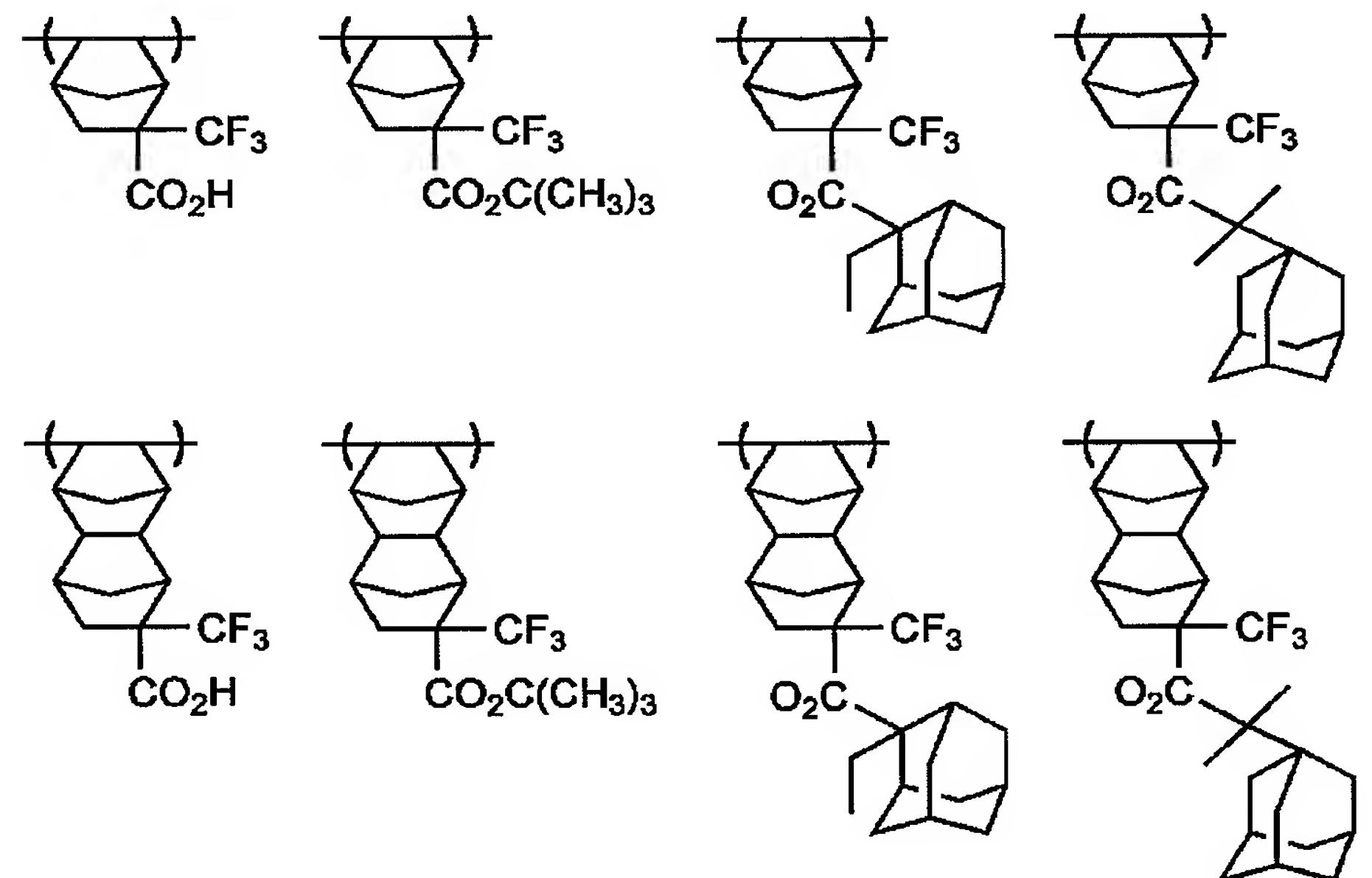
[0039] As a desirable example of the radical from which it is desorbed according to an operation of an acid t-butyl, t-amyl group, a 1-alkyl-1-cyclohexyl radical, A 2-alkyl-2-adamanthyl radical, a 2-adamanthyl-2-propyl group, Acetal radicals, such as the 3rd class alkyl groups, such as a 2-(4-methylcyclohexyl)-2-propyl group, a 1-alkoxy-1-ethoxy radical, a 1-alkoxy-1-methoxy group, and a tetrahydropyranyl group, t-alkyl carbonylmethyl radical, etc. are mentioned preferably. As a radical from which it is desorbed according to an operation of an acid, the 3rd class alkyl group is more desirable, and especially the 3rd class alkyl group that has an alicyclic ring is desirable.

[0040] Although the desirable example of the repeat unit expressed with a general formula (II) is given hereafter, this invention is not limited to this.

[0041]

[Formula 8]

(II)の具体例



[0042] In a general formula (III), R1 expresses a hydrogen atom, a fluorine atom, a chlorine atom, a bromine atom, a cyano group, or a trifluoromethyl radical. even if R41–R46 are the same, they may differ from each

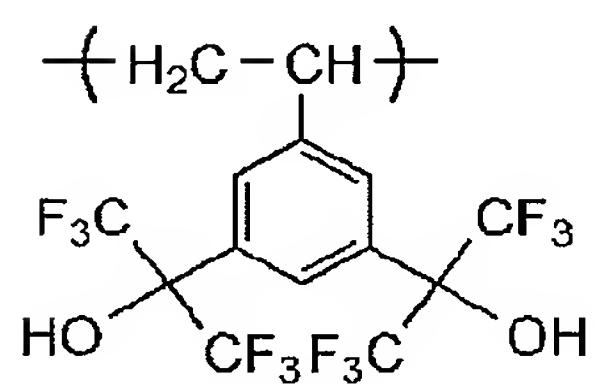
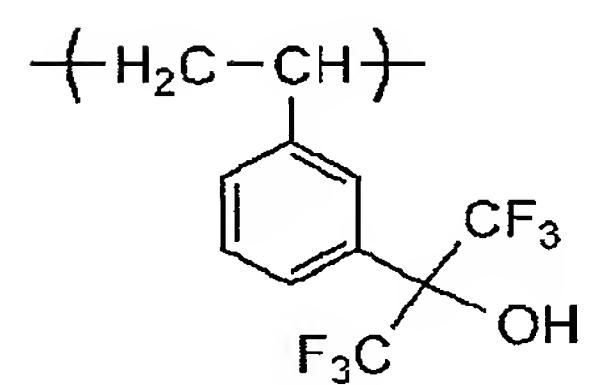
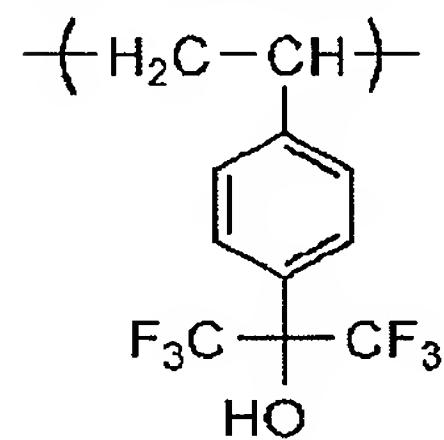
other, and they express a hydrogen atom, a fluorine atom, or a fluoro alkyl group. However, as for R41-R46, all do not serve as a hydrogen atom. n expresses the integer of 1-5. when R41-R46 have two or more n or more by two, respectively, even if each R41-R46 which have more than one are the same, they may differ. [0043] The thing same as a fluoro alkyl group of R41-R46 as the fluoro alkyl group of R11-R16 in a general formula (I) can be mentioned.

[0044] Although the desirable example of the repeat unit expressed with a general formula (III) is given hereafter, this invention is not limited to this.

[0045]

[Formula 9]

(III)の具体例



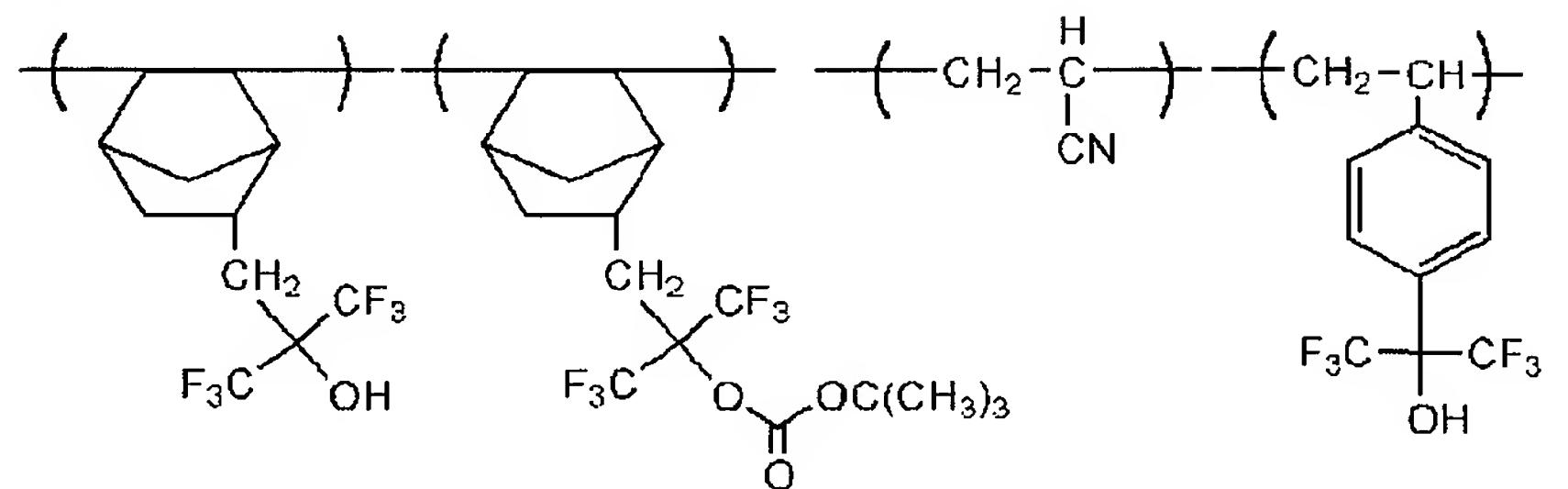
[0046] (B) The resin of a component may carry out the polymerization of other polymerization nature monomers in addition to the above-mentioned repeat unit. As a copolymerization monomer which can be used together For example, acrylic ester, acrylamides, and methacrylic ester, Methacrylamide, an allyl compound, vinyl ether, and vinyl ester The dialkyl ester of styrene, crotonic-acid ester, a maleic acid, or boletic acid A maleic anhydride, maleimide, acrylonitrile, a methacrylonitrile, MAREIRO nitril, C(R1a) (R2a) =C (R1 a-R4a among a formula) (R3a) (R4a) It is the same, but you may differ, and it can mention expressing the alkyl group (preferably 1-10 carbon numbers) which may be permuted by the hydrogen atom, the halogen atom, or the halogen atom etc. Acrylonitrile, a methacrylonitrile, a maleic anhydride, maleimide, N-hydroxy maleimide, N -(t-buthoxycarbonyloxy)- Maleimide and especially C(R1a) (R2a) =C (R3a) (R4a) are desirable. In addition, generally what is necessary is just a copolymerizable addition polymerization nature unsaturated compound.

[0047] Although the desirable example of the resin of the (B) component is given hereafter, this invention is not limited to this.

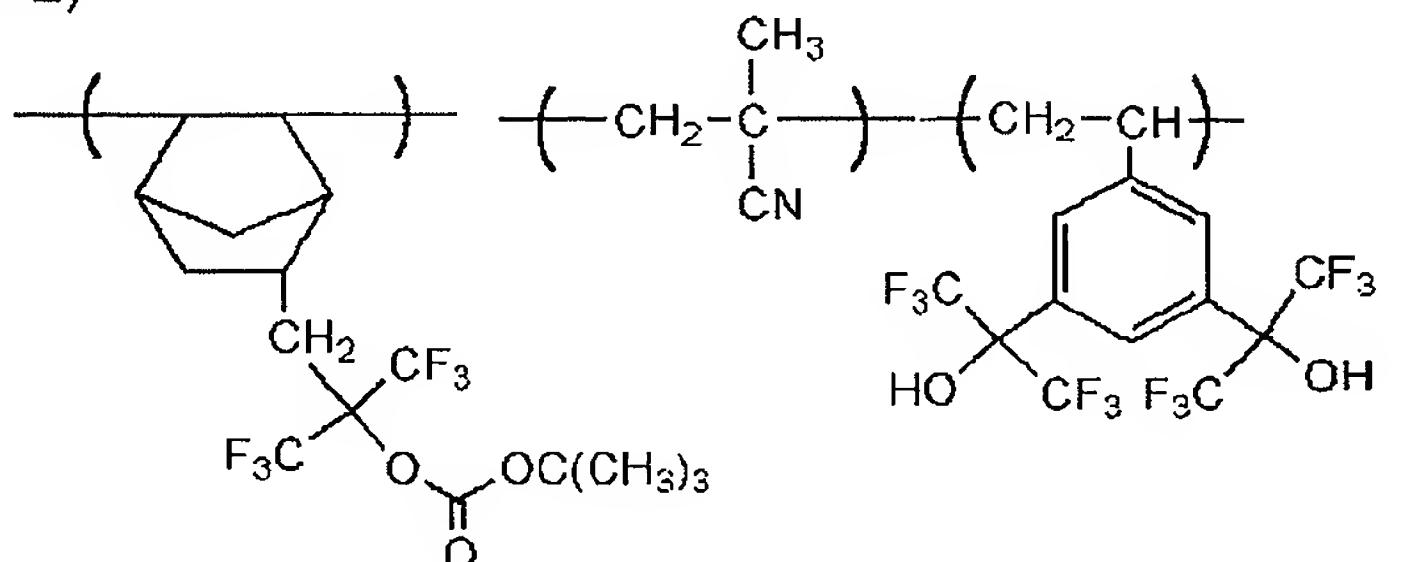
[0048]

[Formula 10]

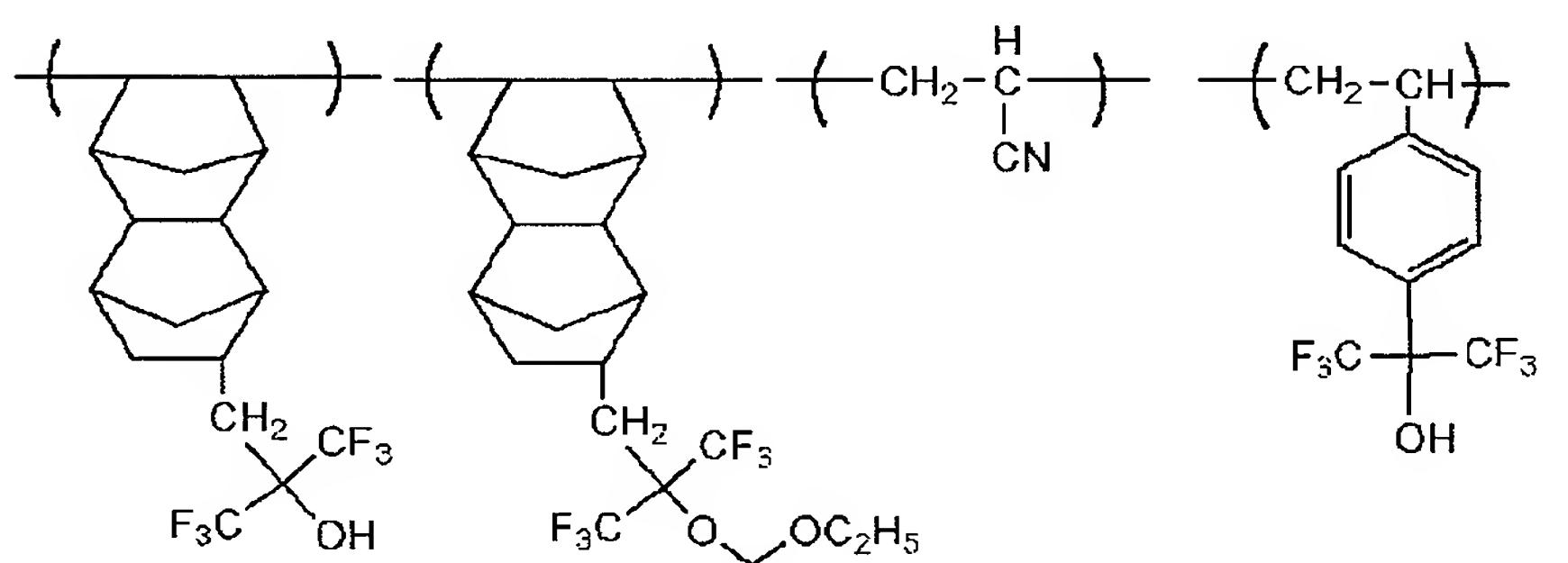
(F-1)



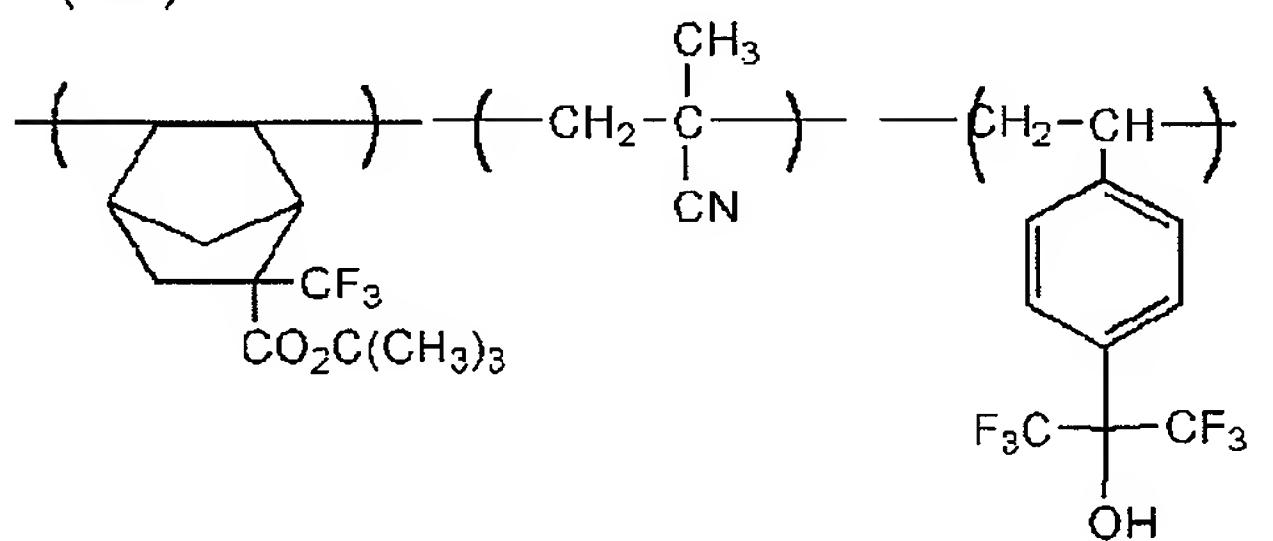
(F-2)



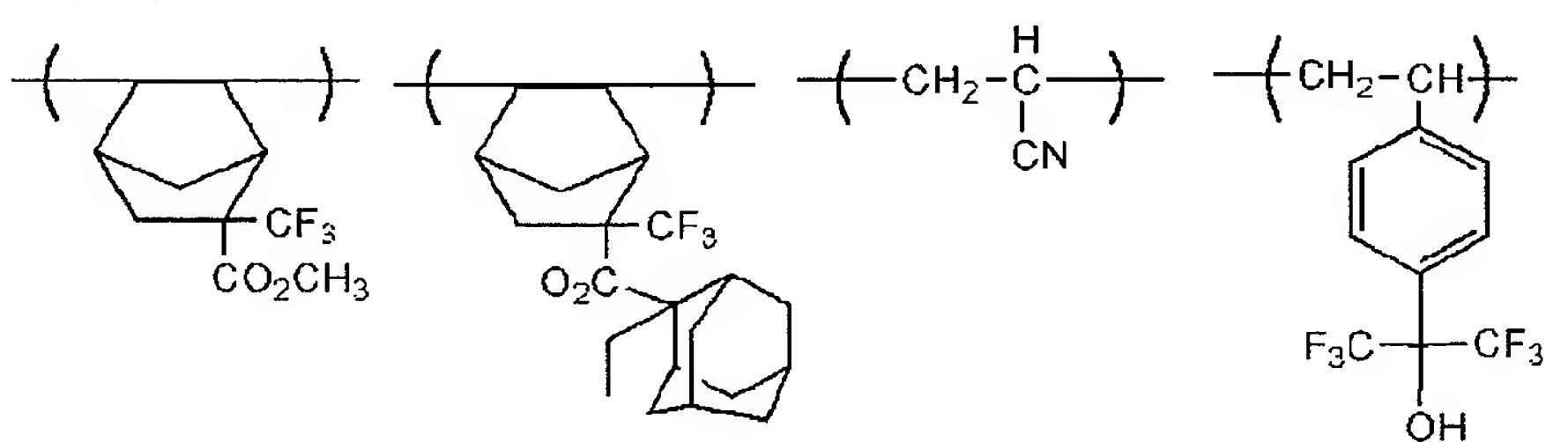
(F-3)



(F-4)



(F-5)



[0049] (B) In the resin of a component, as for the content of the repeat unit expressed with a general formula (I) – (II), it is desirable to consider as 10 – 50-mol %, and it is more desirable to consider as 20 – 30-mol %. (B) In the resin of a component, as for the content of the repeat unit expressed with a general formula (III), it is desirable to consider as 10–40–mol %, and it is more desirable to consider as 20–30–mol %. (B) In the resin of a component, as for the content of the repeat unit which has the radical from which it is desorbed according to an operation of an acidolysis nature machine or an acid, it is desirable to consider as 5–55–mol %, and it is more desirable to consider as 15–35–mol %.

[0050] (B) In a weighted mean, 2000–50000 are desirable still more desirable, and the molecular weight of the resin of a component is 3000–30000. If molecular weight is too low, the thermal resistance of a resist will fall, if too high, the solubility to a developer will worsen and aggravation of sensibility and resolution will be brought about. (B) Being referred to as 1.0–3.0 are 1.1–2.0 desirable still more preferably, and molecular weight degree of dispersion of the resin of a component is 1.1–1.5 especially preferably. After melting the polymer obtained by the usual radical polymerization to a good solvent as an approach of lowering a molecular-weight degree of dispersion, there is an approach by living polymerization methods, such as a method of adding a poor solvent and removing a component with low molecular weight or a living radical polymerization method, and all can be used suitably. All can use the approach using George's and others nitroxide as a living radical polymerization method, the approach of of the Sawamoto and MACHAUFU skiings using a metal complex, etc. Moreover, in a radical polymerization method usual [the viewpoint that the roughness of a pattern improves to / above-mentioned], application of a dropping polymerization method (the approach of a radical polymerization of adding a monomer continuously or intermittently further in case the radical polymerization of the monomer is carried out under existence of a radical polymerization initiator) is desirable. In the dropping polymerization method, even if the class of monomer and presentation which are later added during radical polymerization advance are the same as the class of monomer and presentation which are first taught to a reaction container, they may differ. Moreover, if the approach of adding further with the monomer later added also about a polymerization initiator is used, since the monomer which is unreacted and remains can be reduced, it is desirable.

[0051] (B) Generally the addition of the resin of a component is preferably used in 90 – 98% of the weight of the range still more preferably 80 to 99% of the weight 50 to 99.5% of the weight on the basis of the total solids of a constituent.

[0052] By the exposure of [2] (A) activity beam of light or a radiation, the positive-resist constituent of compound this invention which generates an acid contains especially an activity beam of light or a radiation, and the compound that generates an acid by the exposure of F2 excimer-laser light.

[0053] It can choose from the compounds currently used as a compound (acid generator) which decomposes by the exposure of an activity beam of light or a radiation, and generally generates an acid by the exposure of an activity beam of light or a radiation as a compound which generates an acid. That is, it can be used, choosing from the compounds which generate an acid by a well-known light (400–200nm ultraviolet rays, far ultraviolet rays, especially preferably g line, h line, i line, KrF excimer laser light) currently used for the photoinitiator of optical cationic polymerization, the photoinitiator of an optical radical polymerization, the optical decolorizing agent of coloring matter, optical alterant, or a micro resist, ArF excimer laser light, F2 excimer-laser light, the electron ray, the X-ray, the molecular beam, or the ion beam, and those mixture

suitably.

[0054] as such a compound -- for example -- S.I.Schlesinger, Photogr.Sci.Eng., 18, and 387 (1974) -- Diazonium salt given in T.S.Bal et al, Polymer, 21, 423 (1980), etc., U.S. Pat. No. 4,069,055, said 4,069,056 numbers, ** Re No. 27,992, Ammonium salt given in JP,3-140140,A etc., D.C.Necker et al, Macromolecules, 17, 2468 (1984), C.S.Wen et al, Teh, Proc.Conf.Rad.Curing ASIA, p478 Tokyo, Oct (1988), Phosphonium salt given in U.S. Pat. No. 4,069,055, said 4,069,056 numbers, etc., J.V.Crivello et al, Macromolecules, 10 (6), 1307 (1977), Chem.& Eng.News, Nov.28, p31 (1988), The Europe patent No. 104,143, said 339,049 numbers, 410,201, Iodonium salt given in JP,2-150848,A, JP,2-296514,A, etc., J.V.Crivello et al, Polymer J.17, 73 (1985), J.V.Crivello et al., J.Org.Chem., 43, 3055 (1978), W.R.Watt et al, J.Polymer Sci., PolymerChem.Ed., 22, 1789 (1984), J.V.Crivello et al, Polymer Bull., 14, 279 (1985), J.V.Crivello et al, Macromolecules, 14 (5), 1141 (1981), J.V.Crivello et al, J.Polymer Sci., Polymer Chem.Ed., 17, 2877 (1979), The Europe patent No. 370,693, said 161,811 numbers, said 410,201 numbers, said -- No. 339,049 -- said -- No. 233,567 -- said -- No. 297,443 -- said -- No. 297,442 U.S. Pat. No. 4,933,377, said 3,902,114 numbers, said 4,760,013 numbers, Said 4,734,444 numbers, said 2,833,827 numbers, the Germany patent No. 2,904,626, Sulfonium salt given in said 3,604,580 numbers, said 3,604,581 numbers, etc., J.V.Crivello et al, Macromolecules, 10 (6), A seleno NIUMU salt given in 1307 (1977), J.V.Crivello et al, J.Polymer Sci., Polymer Chem.Ed., 17, 1047 (1979), etc., Onium salt, such as arsonium salt given in C.S.Wen et al, Teh, Proc.Conf.Rad.Curing ASIA, p478 Tokyo, Oct (1988), etc., U.S. Pat. No. 3,905,815, JP,46-4605,B, JP,48-36281,A, JP,55-32070,A, JP,60-239736,A, JP,61-169835,A, JP,61-169837,A, JP,62-58241,A, JP,62-212401,A, An organic halogenated compound given in JP,63-70243,A, JP,63-298339,A, etc., K.Meier et al, J.Rad.Curing, 13 (4), 26 (1986), T.P.Gill et al, Inorg.Chem., 19, 3007 (1980), D.Astruc, Acc.Chem.Res., 19 (12), An organic metal / organic halogenide given in 377 (1896), JP,2-161445,A, etc., S.Hayase et al, J.Polymer Sci., 25,753 (1987), E. Reichmanis et al, J.PolymerSci., Polymer Chem.Ed., 23, 1 (1985), Q.Q.Zhu et al, J.Photochem., 36, 85, 39, 317 (1987), B.Amit et al, Tetrahedron Lett., (24) 2205 (1973), D.H.R.Barton et al, J.Chem Soc., 3571 (1965), P.M.Collins et al, J.Chem.Soc., Perkin I, 1695 (1975), M.Rudinstei et al and Tetrahedron Lett., (17), 1445 (1975), J.W.Walker et al, J.Am.Chem.Soc., 110, 7170 (1988), S.C.Busman et al, J.Imaging Technol., 11 (4), 191 (1985), H.M.Houlihan et al, Macromolecules, 21, 2001 (1988), P.M.Collins et al, J.Chem.Soc., Chem.Commun., 532 (1972), S.Hayase et al, Macromolecules, 18, 1799 (1985), E.Reichmanis et al, J.Electrochem.Soc., Solid State Sci.Technol., 130 (6), F.M.Houlihan et al, Macromolecules, 21, 2001 (1988), the Europe patent 0290th and No. 750 -- said -- No. 046 or 083 -- said -- No. 156 or 535 Said 271,851 numbers, said 0,388,343 numbers, U.S. Pat. No. 3,901,710, The photo-oxide generating agent which has 0-nitrobenzyl mold protective group of a publication in said 4,181,531 numbers, JP,60-198538,A, JP,53-133022,A, etc., M. TUNOOKA et al, Polymer Preprints Japan, 35 (8), G.Berner et al, J.Rad.Curing, 13 (4), W.J.Mijs et al, Coating Technol., 55 (697), 45 (1983), Akzo, H.Adachi et al, Polymer Preprints, Japan, 37 (3), the Europe patent 0199th and No. 672 -- said -- No. 84515 -- said -- No. 044 or 115 said -- No. 618,564 -- said -- No. 0101 or 122 and U.S. Pat. No. 4,371,605 -- said -- 4,431,774 a number, JP,64-18143,A, and JP,2-245756,A -- The disulfon compound of a publication etc. can be mentioned to a compound which photodissociates and generates a sulfonic acid, JP,61-166544,A, etc. which are represented by imino sulfonate given in JP,3-140109,A etc.

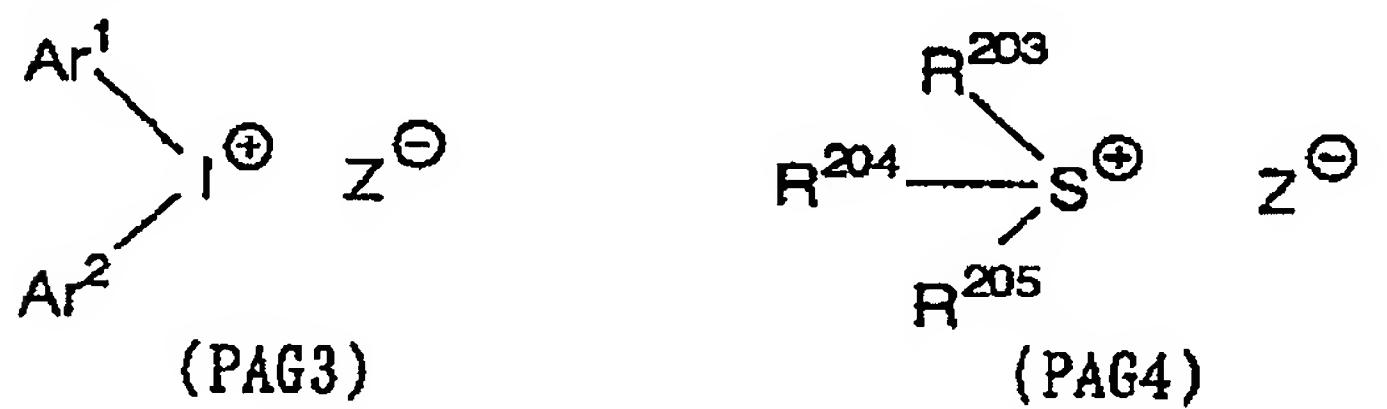
[0055] In this invention, the compound (A1) which generates an organic sulfonic acid by the exposure of an activity beam of light or a radiation is desirable as a compound which generates an acid by the exposure of

an activity beam of light or a radiation. As a compound (A1) which generates an organic sulfonic acid by the exposure of an activity beam of light or a radiation, the compound (A1a) which generates a fluorine content sulfonic acid by the exposure of an activity beam of light or a radiation, and the compound (A1b) which generates fluorine a non-containing sulfonic acid by the exposure of an activity beam of light or a radiation can be mentioned.

[0056] (A1a) As a compound which generates a fluorine content sulfonic acid by the exposure of the compound activity beam of light or radiation which generates a fluorine content sulfonic acid by the exposure of an activity beam of light or a radiation, the iodonium salt expressed with the following general formula (PAG3) or the sulfonium salt expressed with a general formula (PAG4) can be mentioned, for example.

[0057]

[Formula 11]



[0058] Ar1 and Ar2 show respectively the aryl group which is not permuted [a permutation or] independently among a formula. R203, R204, and R205 show respectively the alkyl group which is not permuted [a permutation or] and an aryl group independently. Z⁻ shows the sulfonic-acid anion which has at least one fluorine atom. Moreover, two, and Ar1 and Ar2 of R203, R204, and R205 may be combined through each single bond or substituent.

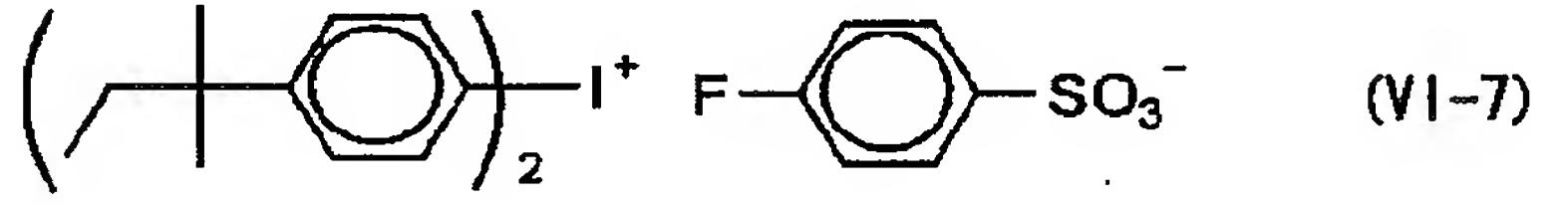
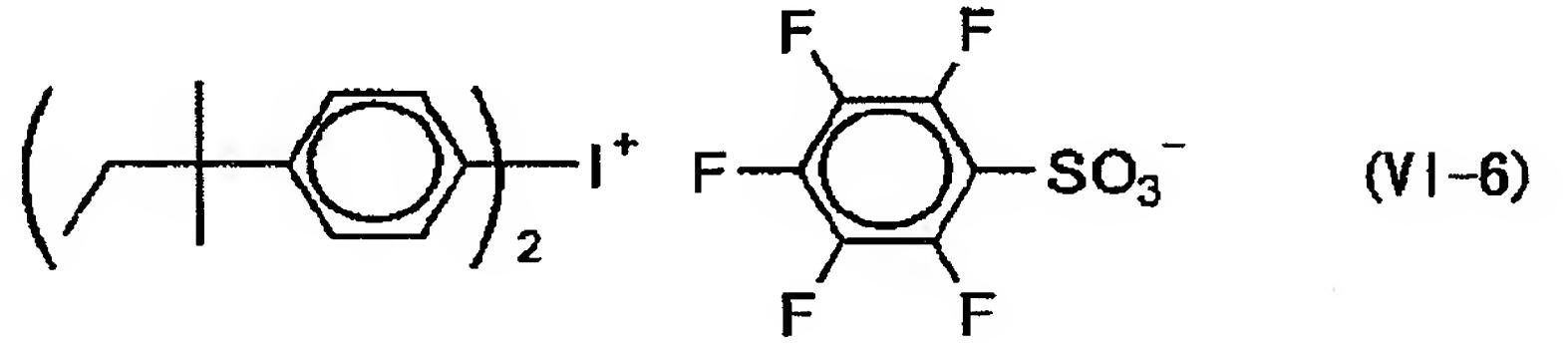
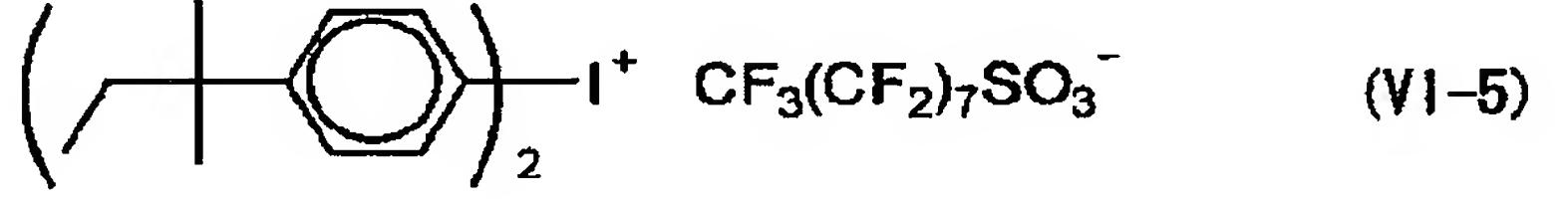
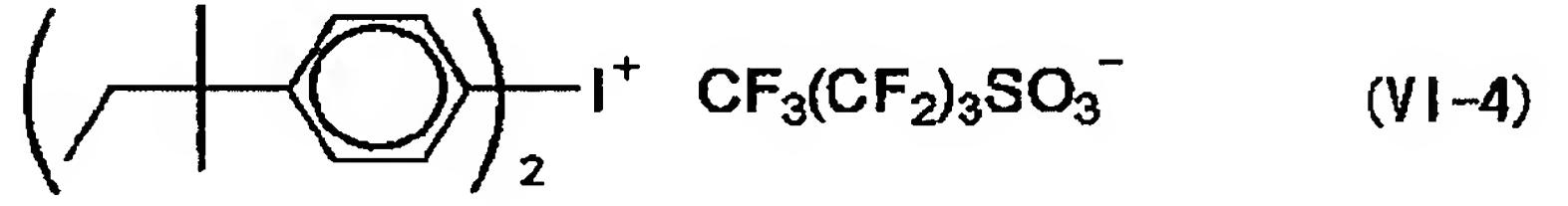
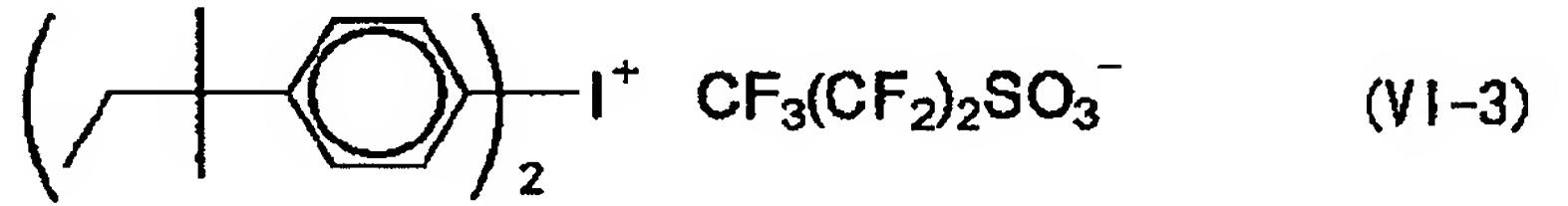
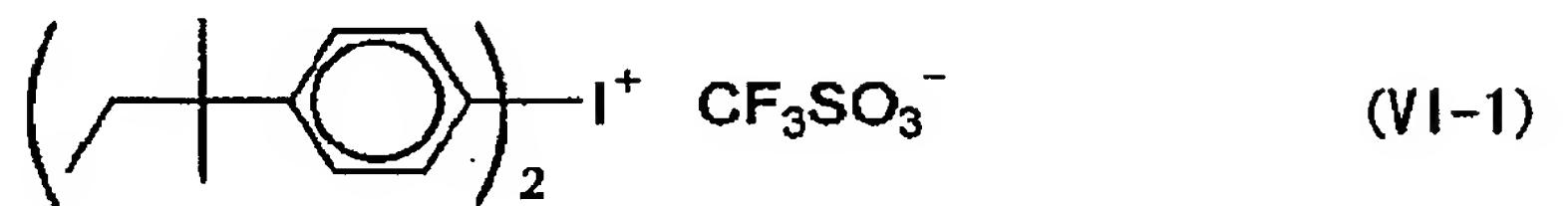
[0059] As an aryl group as Ar1, Ar2, R203, R204, and R205, it is the alkyl group of carbon numbers 1–8 preferably [it is desirable and] as the aryl group of carbon numbers 6–14, and an alkyl group. As a desirable substituent, to an aryl group, it is the alkoxy group of carbon numbers 1–8, the alkyl group of carbon numbers 1–8, the alkoxy carbonyl group of carbon numbers 2–9, the alkyl carbonylamino radical of carbon numbers 2–9, a nitro group, a carboxyl group, a hydroxy group, a halogen atom, and a phenylthio radical, and the alkoxy group of carbon numbers 1–8, the aryl group of carbon numbers 5–14, the aryl carbonyl group of carbon numbers 6–15, a carboxyl group, and a halogen atom can be mentioned to an alkyl group.

[0060] As a sulfonic-acid anion of Z-, the aliphatic hydrocarbon of the carbon numbers 1-20 which have at least one fluorine atom, and the aromatic hydrocarbon of carbon numbers 5-20 can be mentioned preferably. These may have the substituent and can mention as a substituent the alkoxy group in which carbon numbers 1-10 may be carrying out the fluorine permutation, the alkoxy carbonyl group in which carbon numbers 2-11 may be carrying out the fluorine permutation, a phenylamino radical, a phenyl carbonyl group, a halogen atom, and a hydroxyl group, for example. To aromatic hydrocarbon, the alkyl group of carbon numbers 1-15 can be mentioned further. In addition, especially about an aliphatic series sulfonic-acid anion, the anion which has a fluorine atom on alpha carbon atom of a sulfonic acid has high acid strength, and is in the inclination to perform salt exchange easily to the anion which does not have a fluorine atom. Moreover, a perfluoro aliphatic series sulfonic acid has still higher acid strength.

[0061] Although an example is given to below, it is not limited to these.

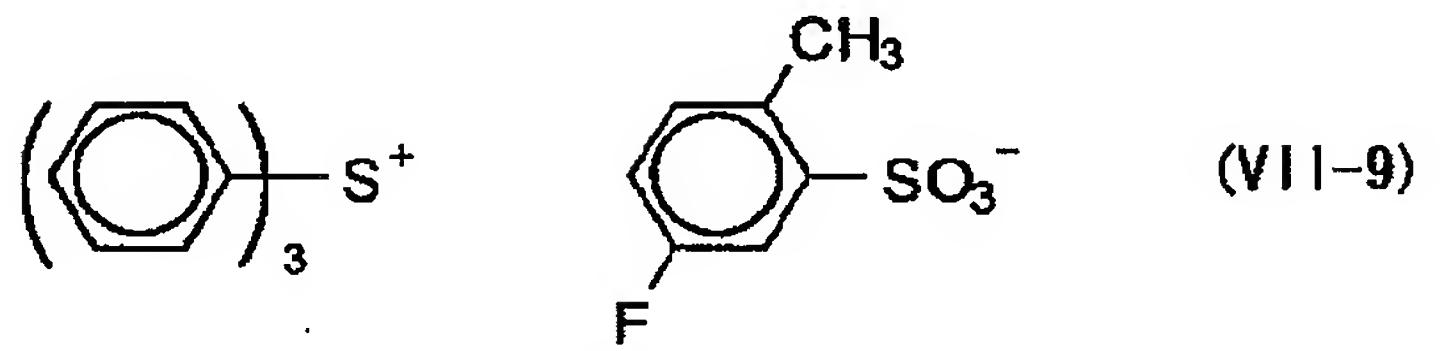
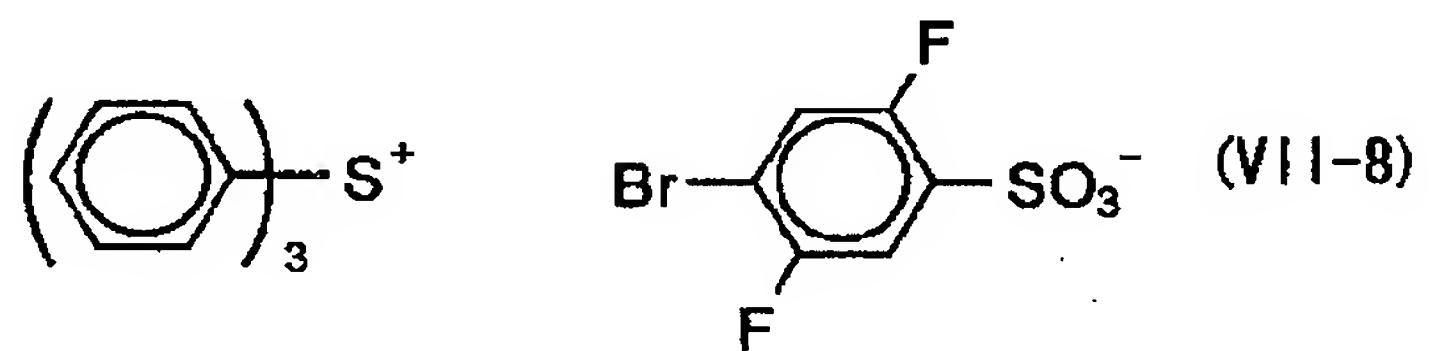
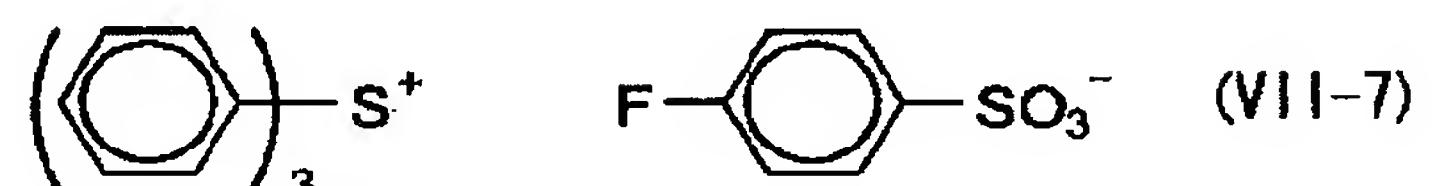
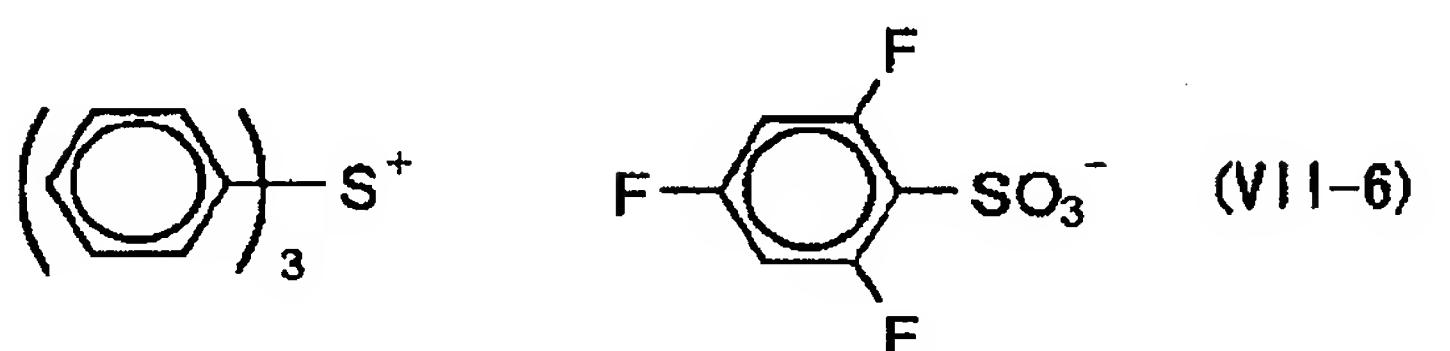
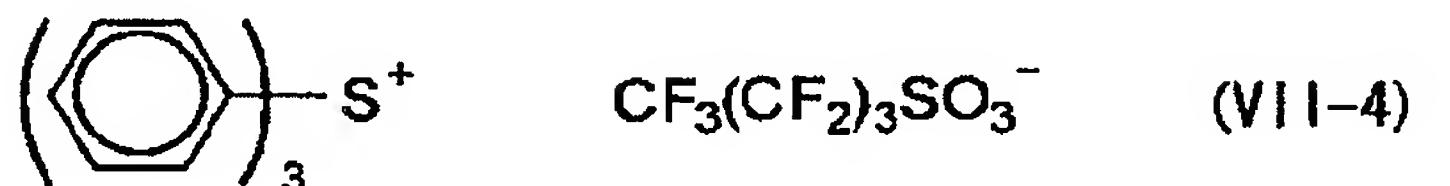
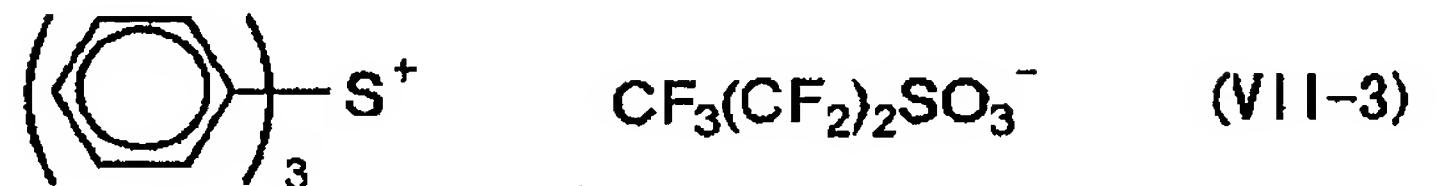
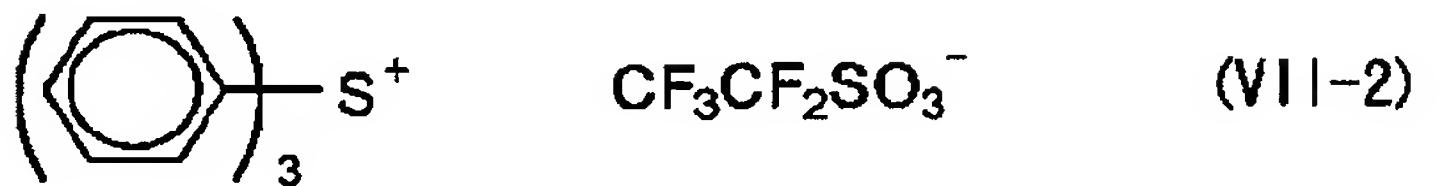
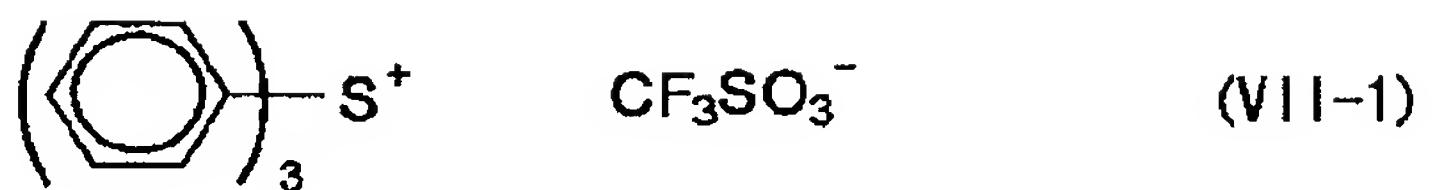
[0062]

[Formula 12]



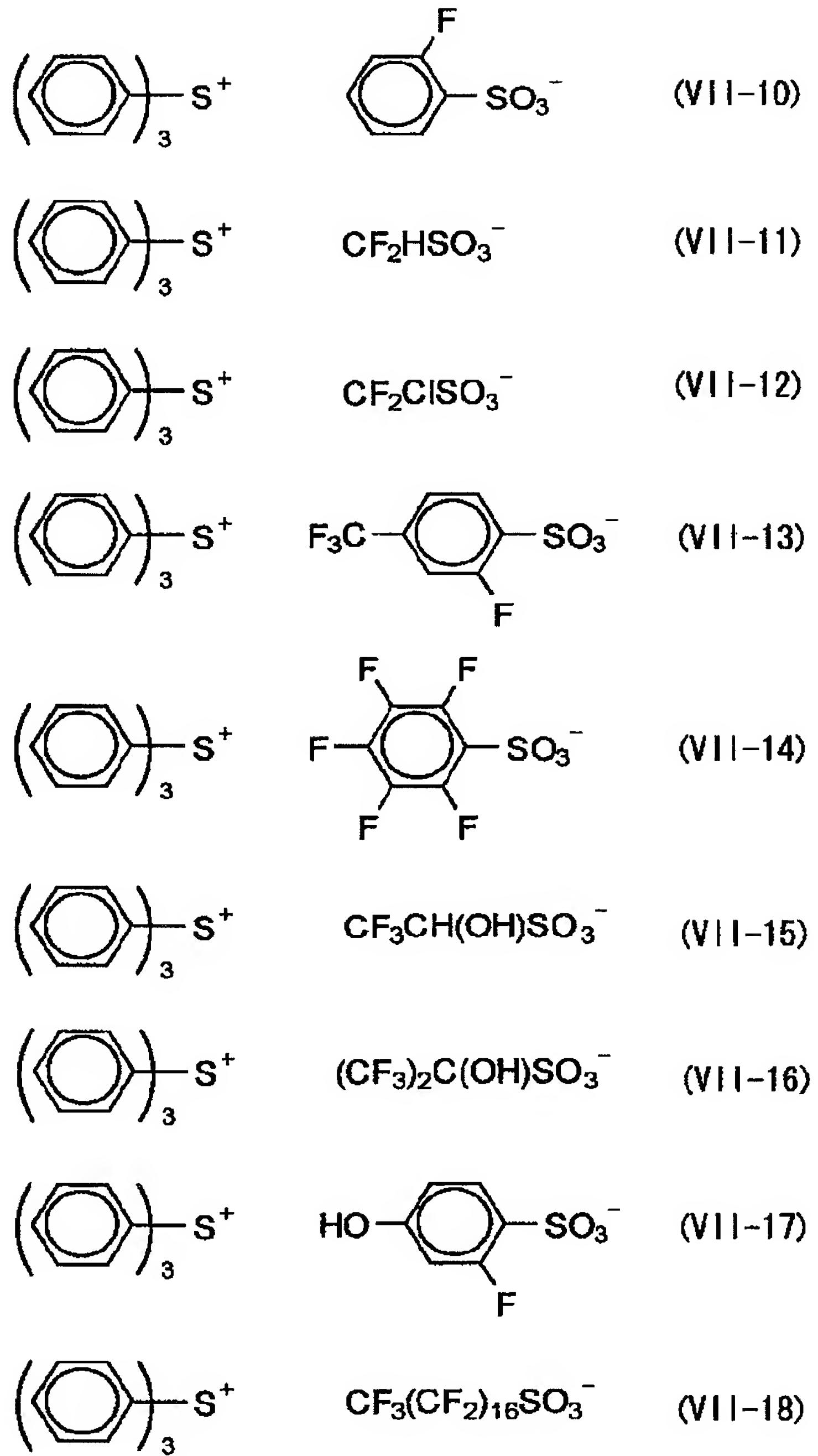
[0063]

[Formula 13]



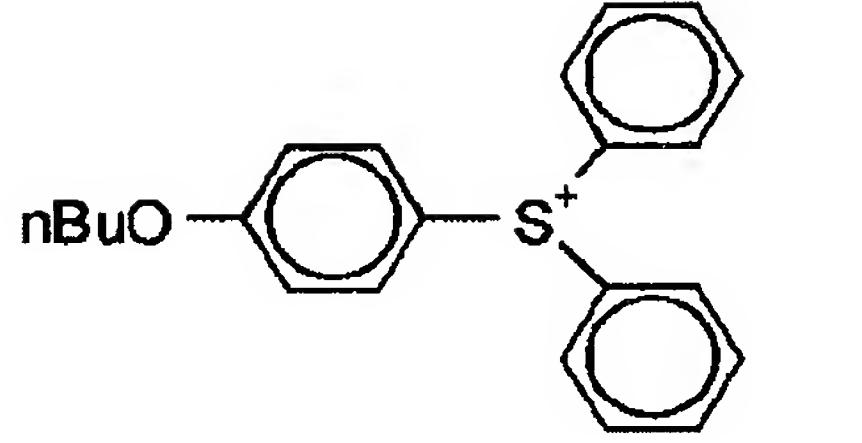
[0064]

[Formula 14]

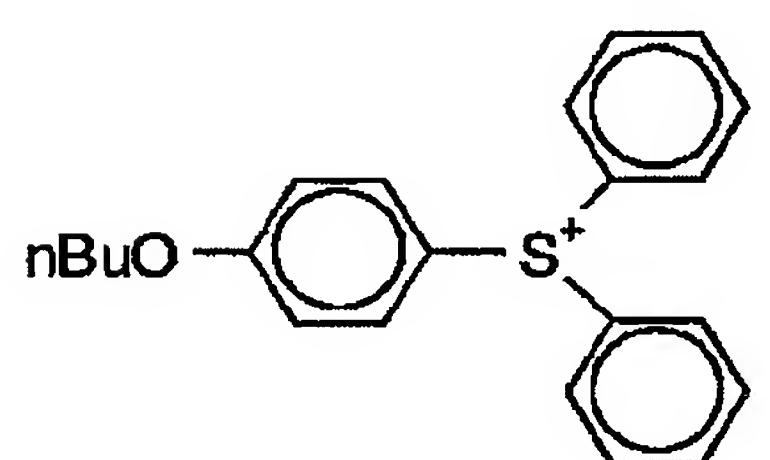


[0065]

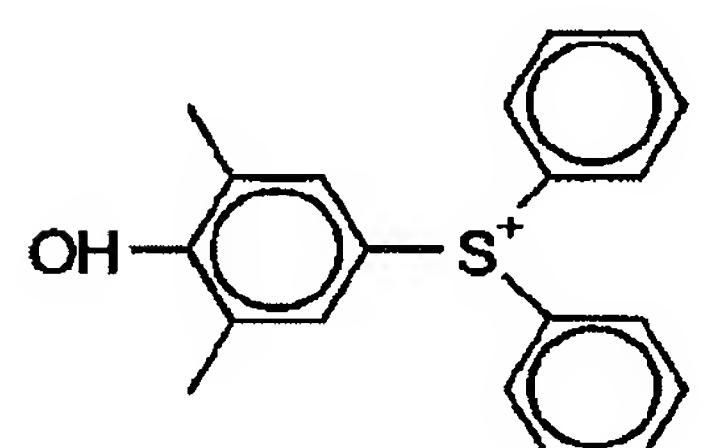
[Formula 15]



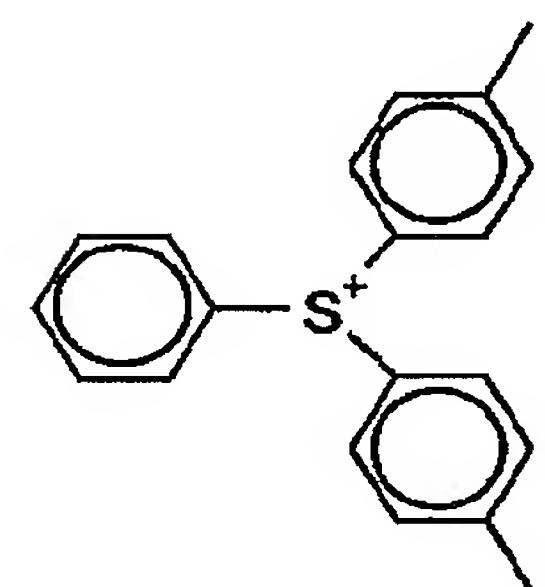
$\text{CF}_3\text{CFHSO}_3^-$ (VII-19)



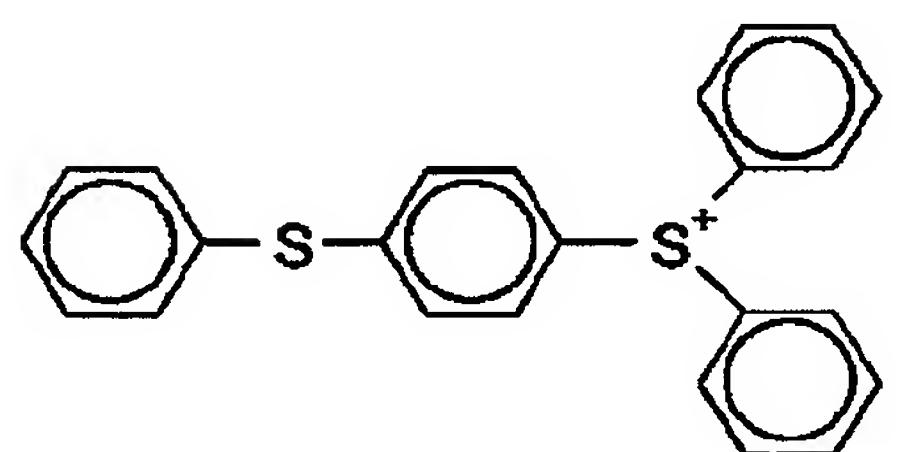
$\text{F}-\text{C}_6\text{H}_3\text{F}-\text{SO}_3^-$ (VII-20)



$\text{CF}_3(\text{CF}_2)_2\text{SO}_3^-$ (VII-21)



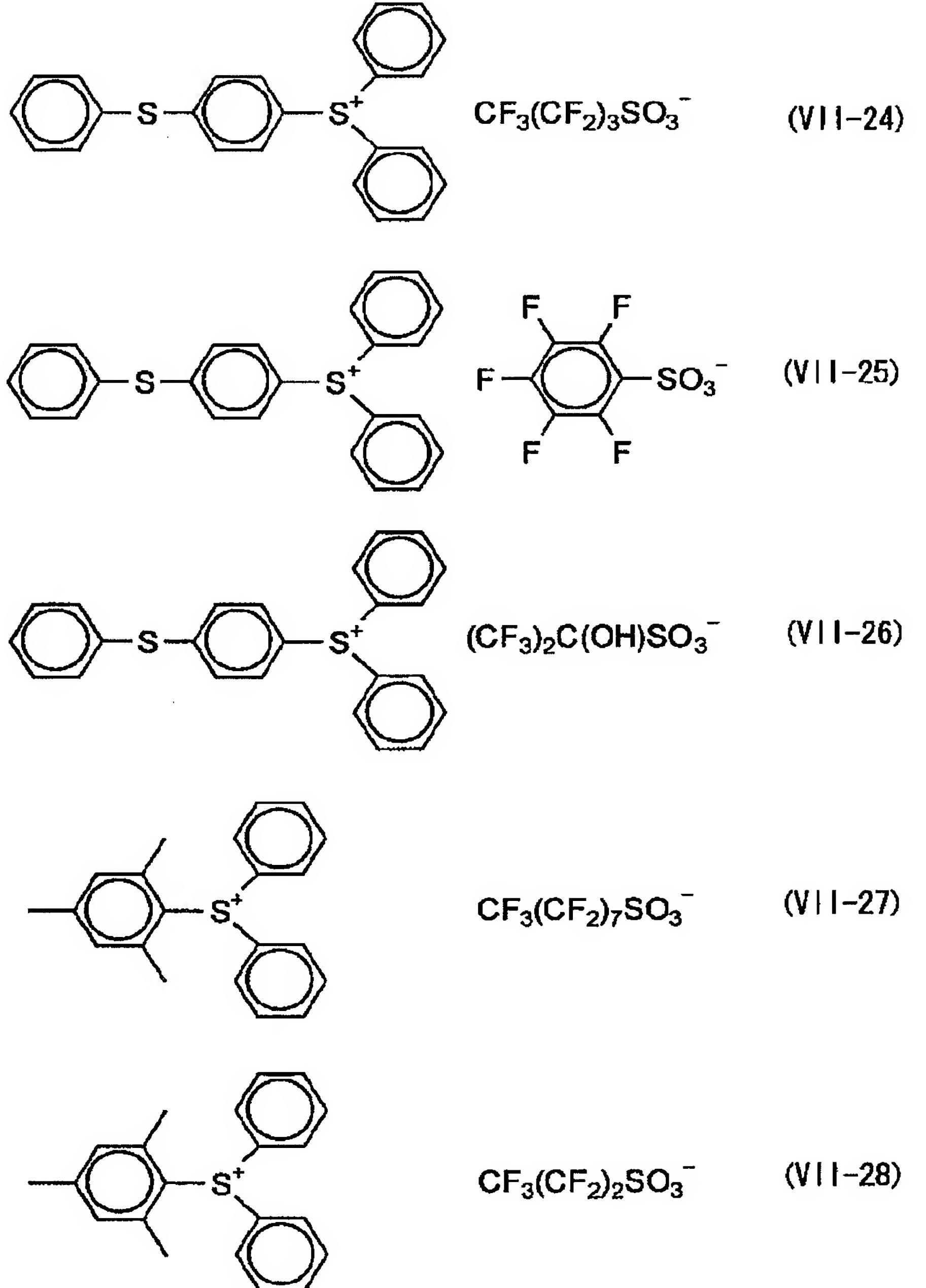
$\text{CF}_3(\text{CF}_2)_3\text{SO}_3^-$ (VII-22)



CF_3SO_3^- (VII-23)

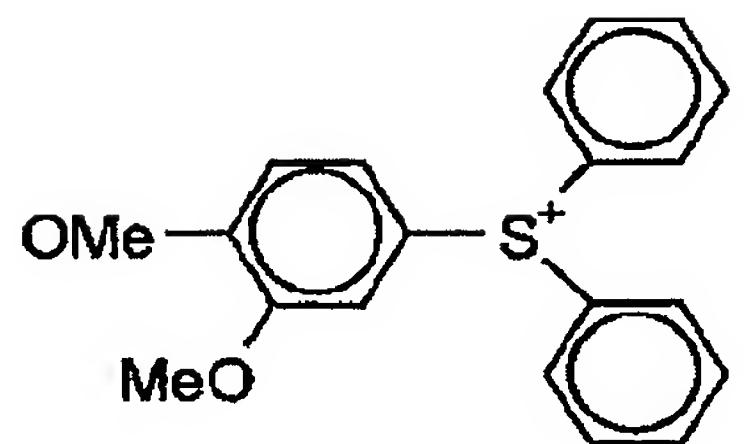
[0066]

[Formula 16]

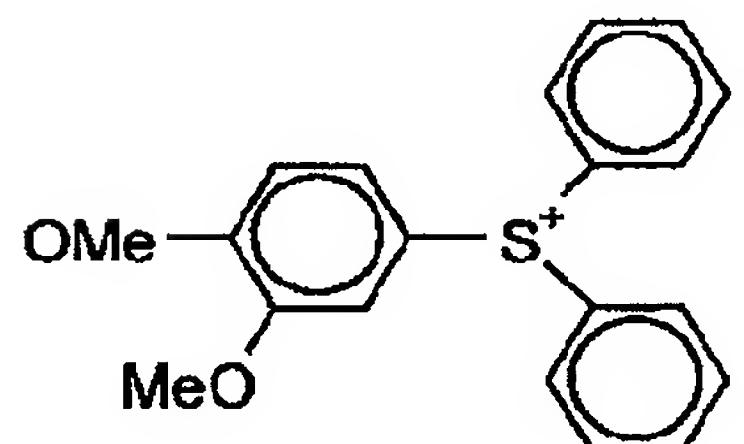


[0067]

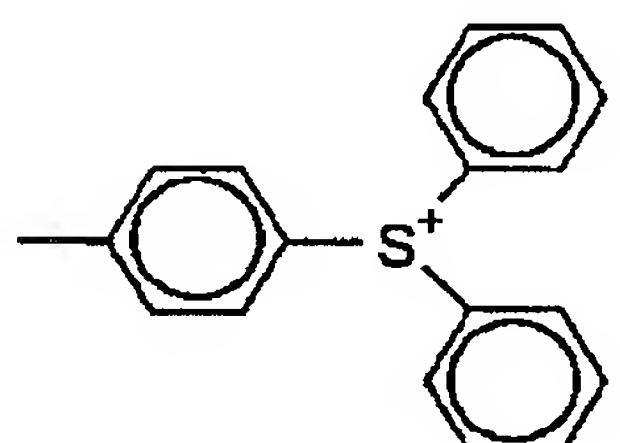
[Formula 17]



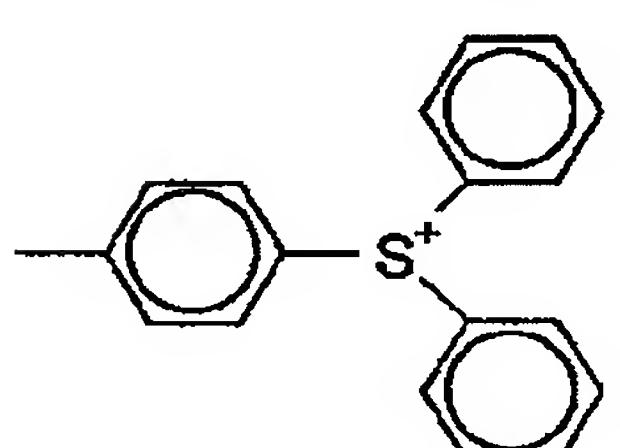
$\text{CF}_2\text{ClSO}_3^-$ (VII-29)



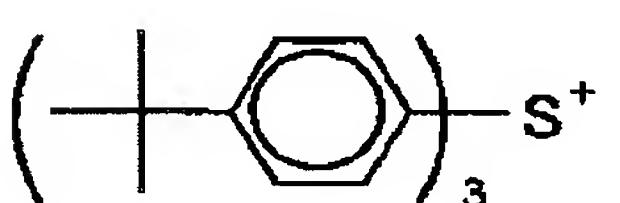
$\text{CF}_3(\text{CF}_2)_3\text{SO}_3^-$ (VII-30)



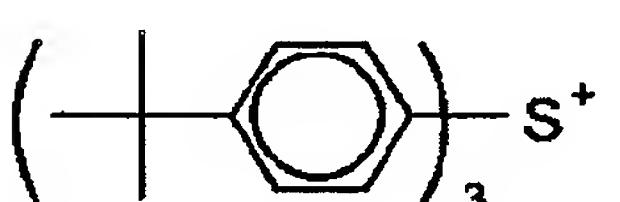
$\text{CF}_3(\text{CF}_2)_2\text{SO}_3^-$ (VII-31)



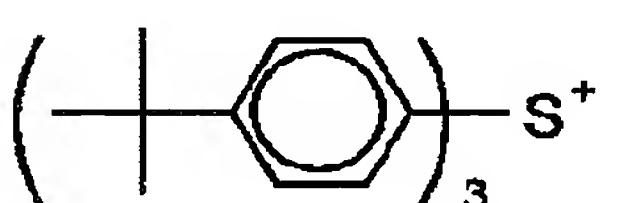
$\text{CF}_3(\text{CF}_2)_2\text{SO}_3^-$ (VII-32)



CF_3SO_3^- (VII-33)



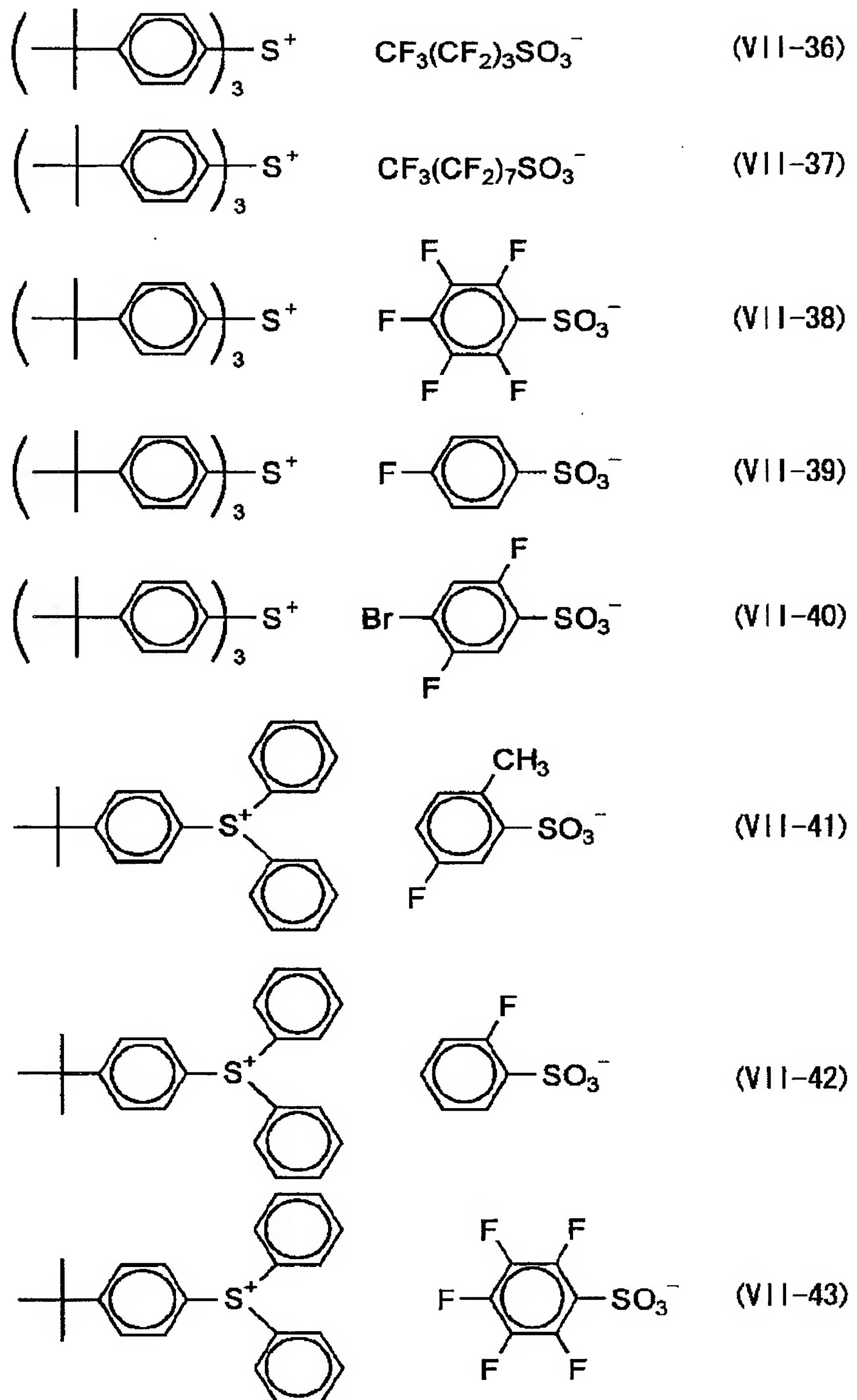
$\text{CF}_2\text{HSO}_3^-$ (VII-34)



$\text{CF}_3(\text{CF}_2)_2\text{SO}_3^-$ (VII-35)

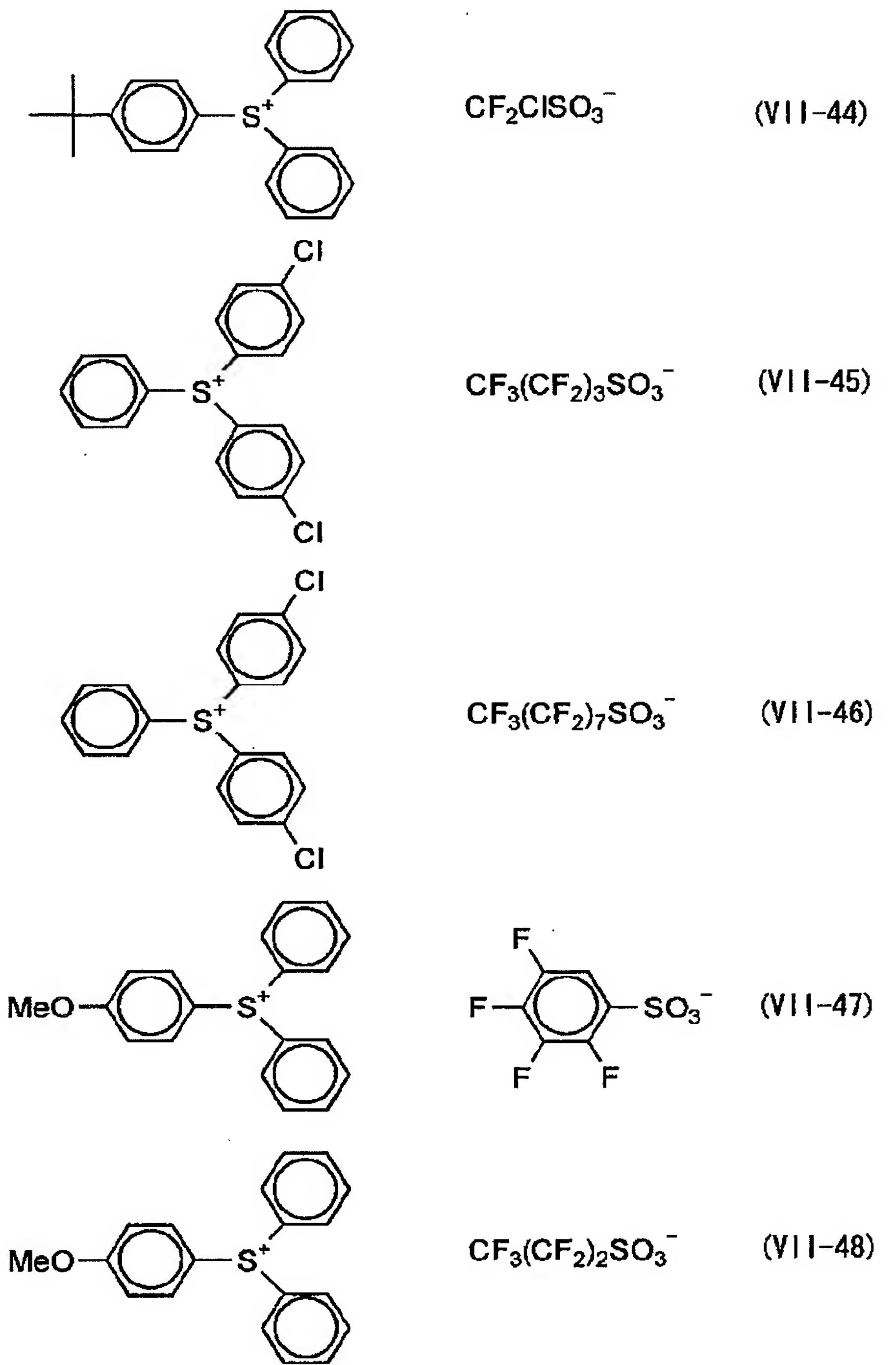
[0068]

[Formula 18]



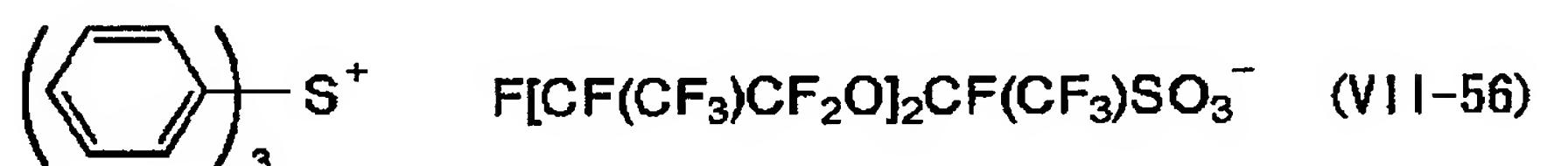
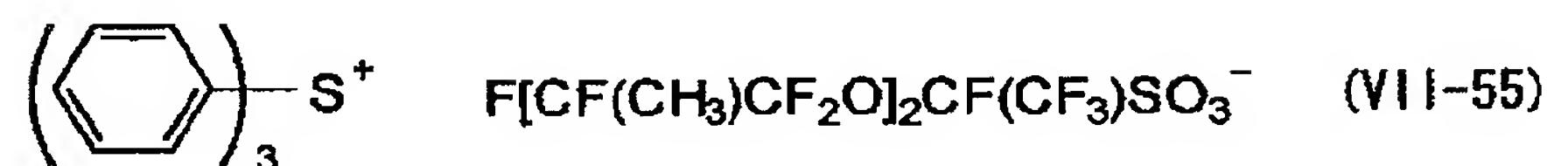
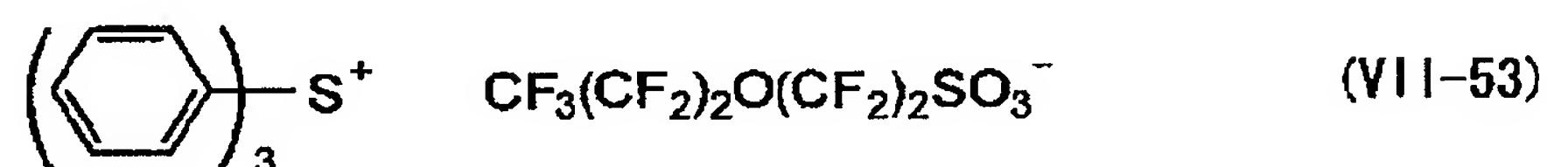
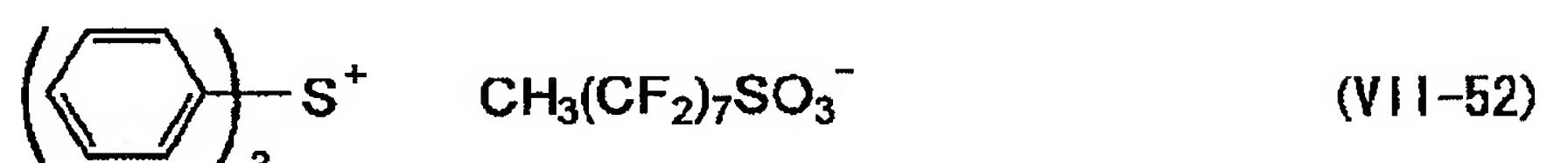
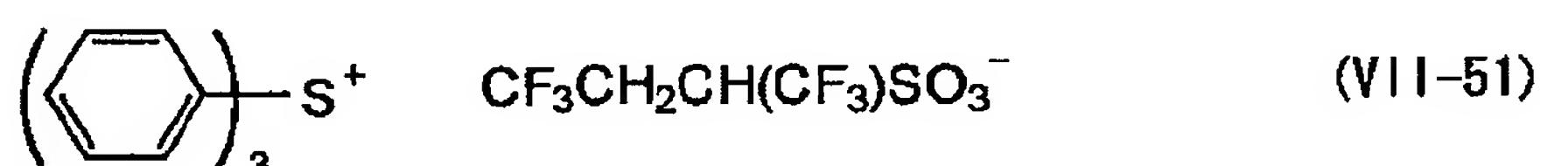
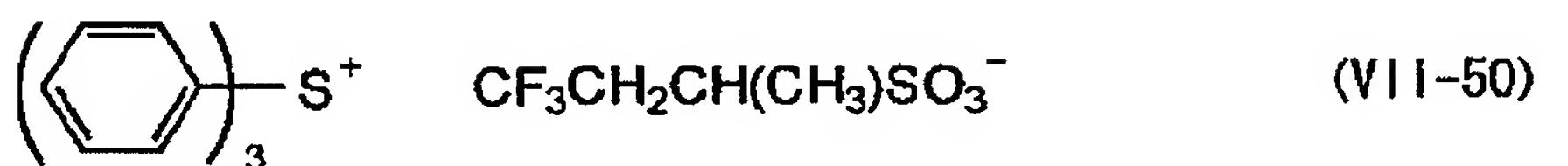
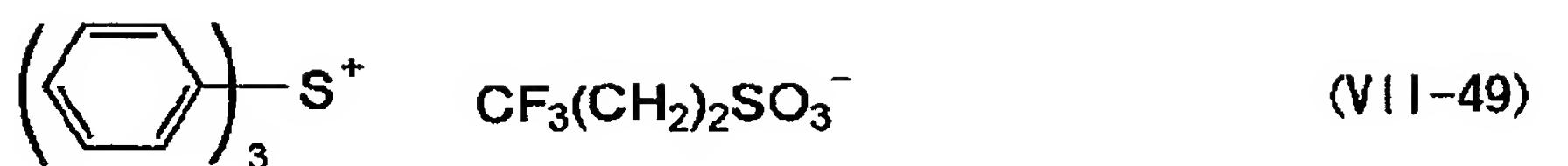
[0069]

[Formula 19]



[0070]

[Formula 20]

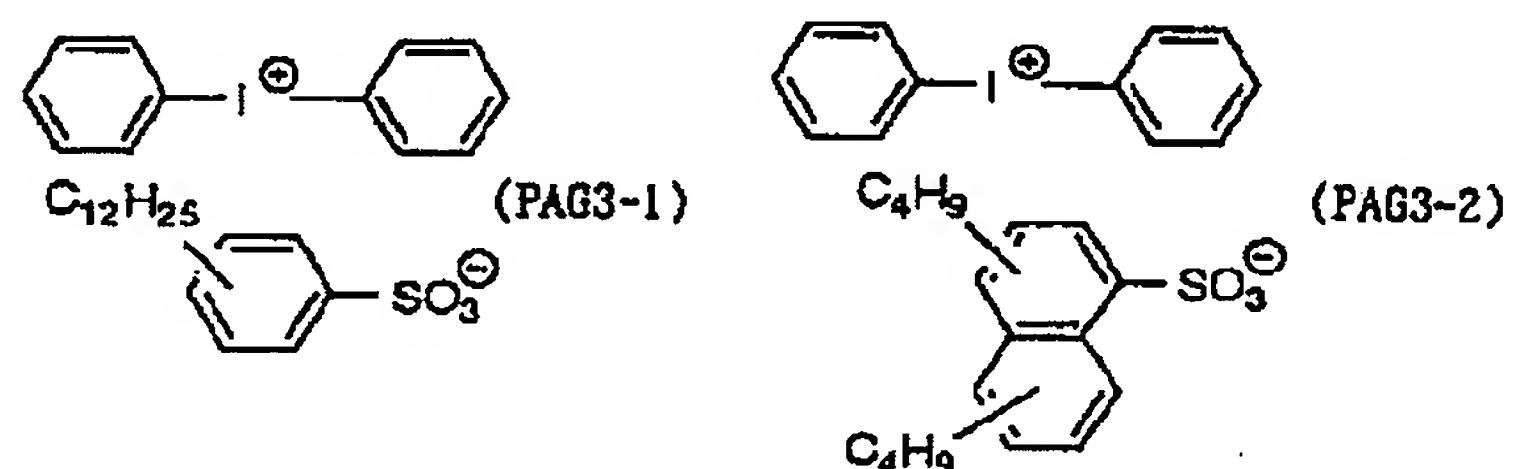


[0071] (A1b) As a compound which generates fluorine a non-containing sulfonic acid by the exposure of the compound activity beam of light or radiation which generates fluorine a non-containing sulfonic acid by the exposure of an activity beam of light or a radiation, the iodonium salt and sulfonium salt which are a previous general formula (PAG3) and (PAG4) the sulfonic-acid anion in which it sets and Z^- does not have a fluorine atom can be mentioned, for example.

[0072] Although the compound shown below as an example is mentioned, it is not limited to these.

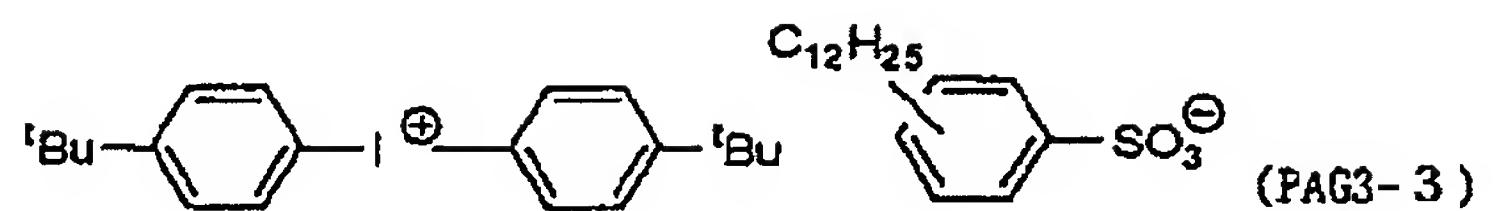
[0073]

[Formula 21]



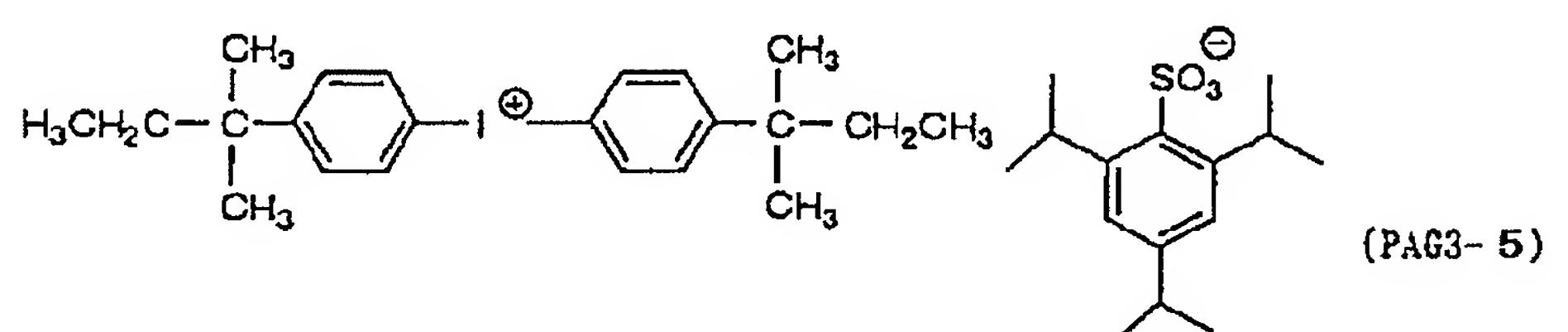
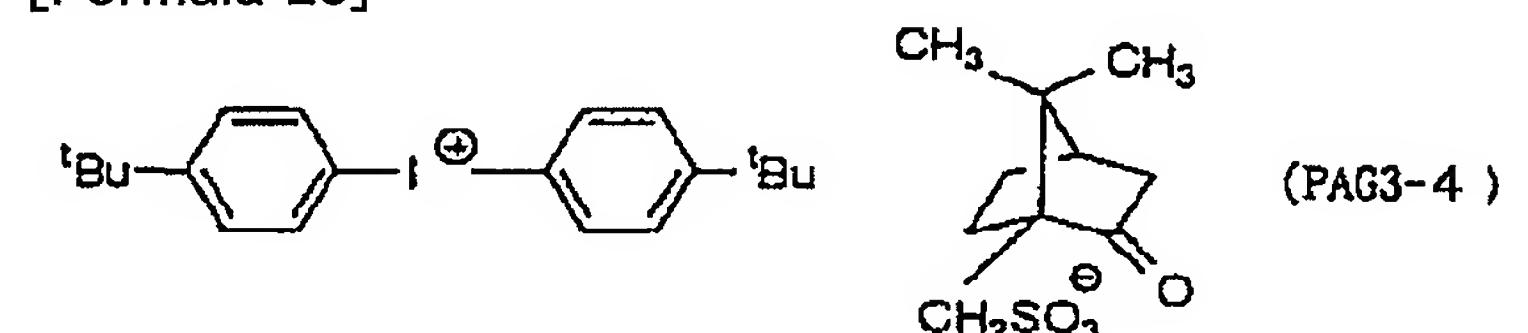
[0074]

[Formula 22]



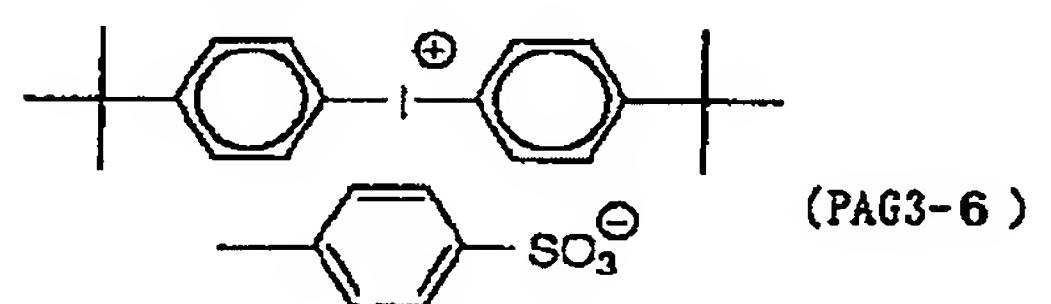
[0075]

[Formula 23]



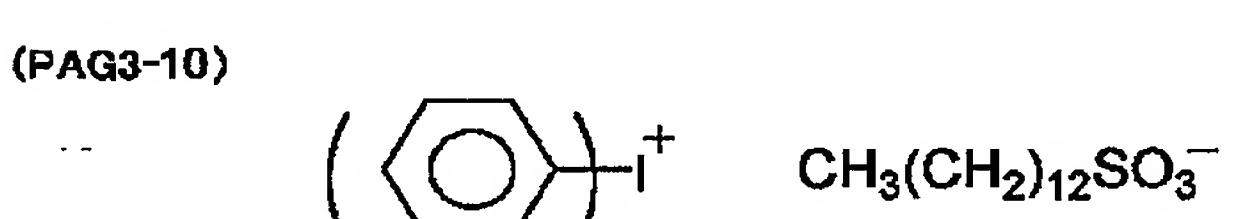
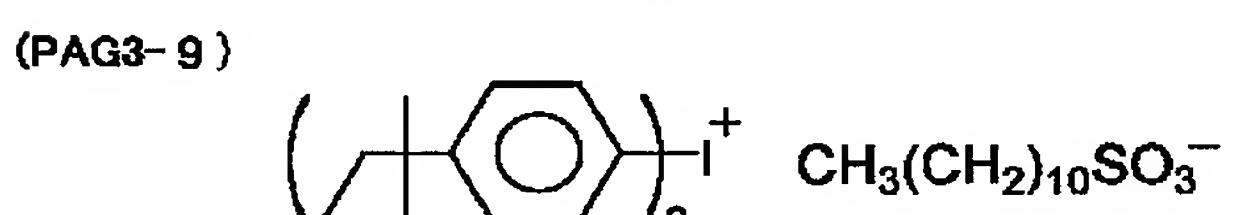
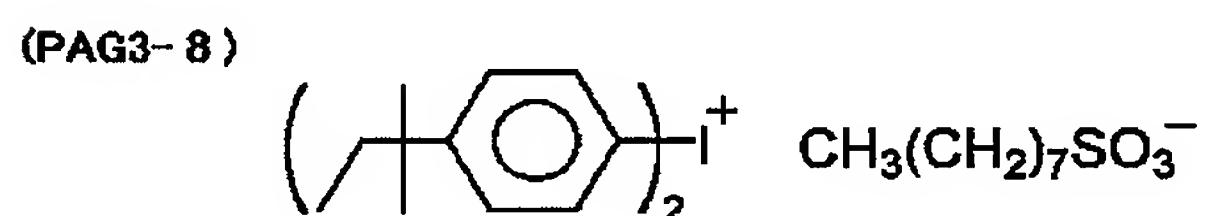
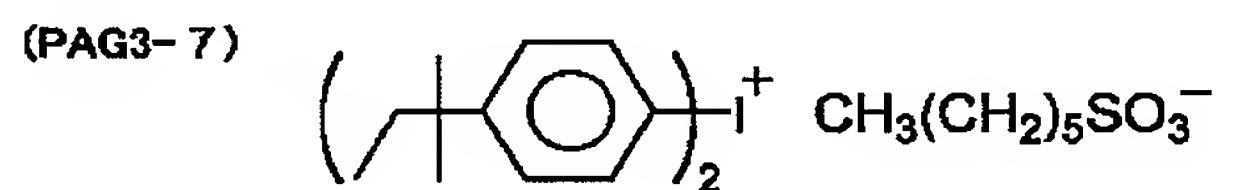
[0076]

[Formula 24]



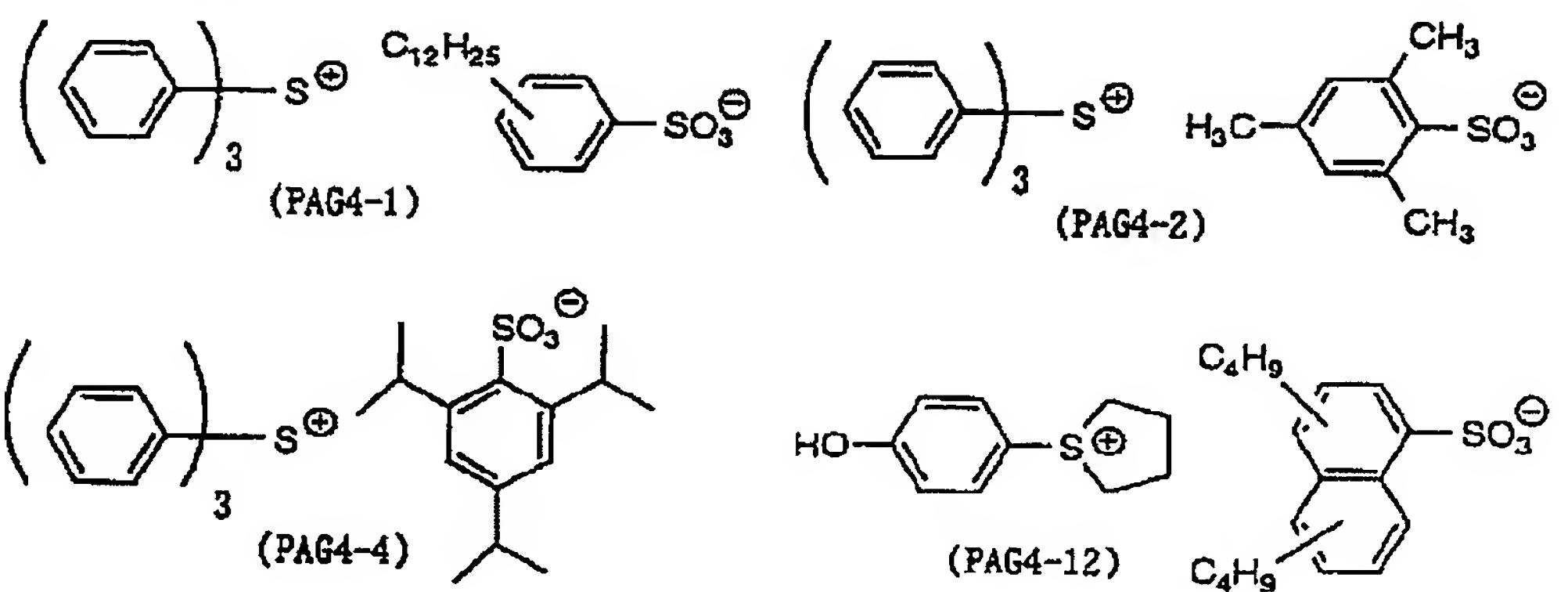
[0077]

[Formula 25]



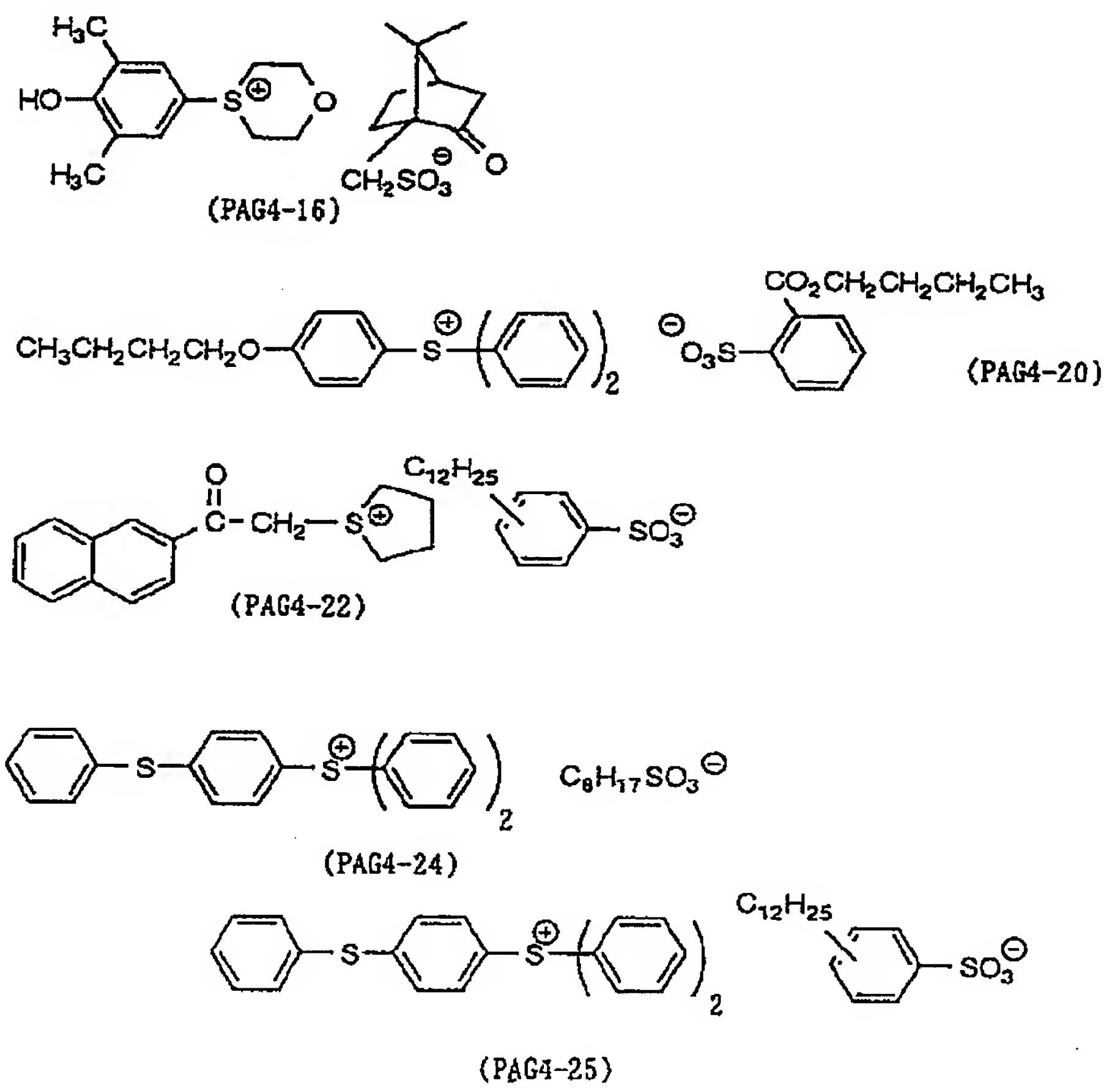
[0078]

[Formula 26]



[0079]

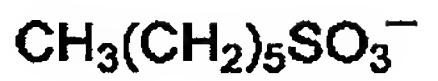
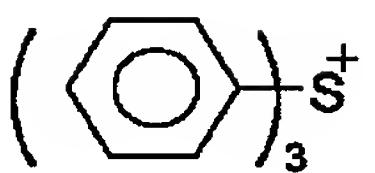
[Formula 27]



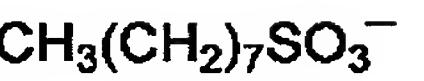
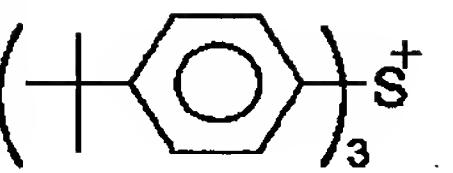
[0080]

[Formula 28]

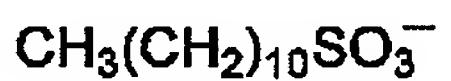
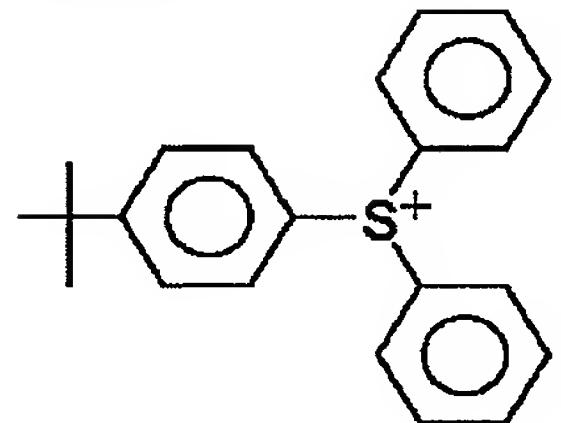
(PAG4-33)



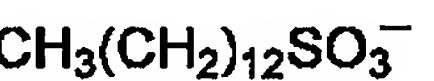
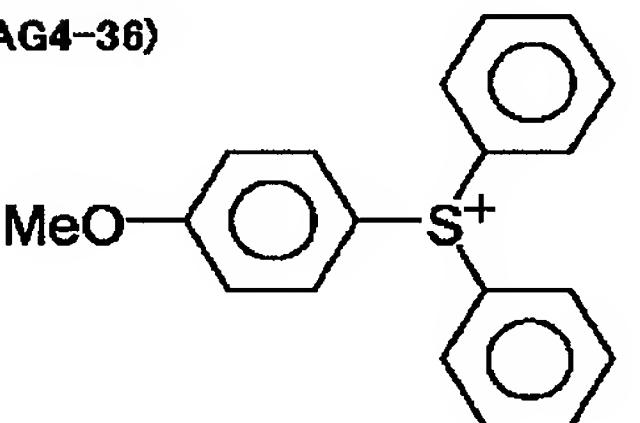
(PAG4-34)



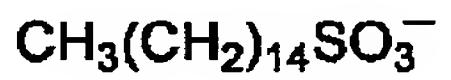
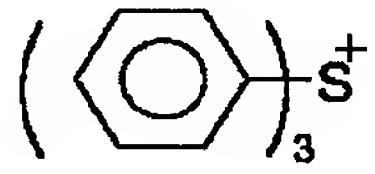
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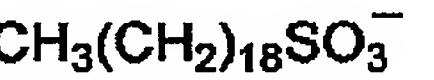
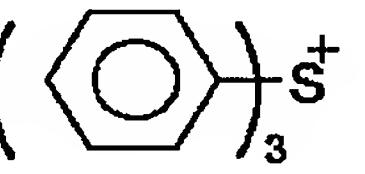
(PAG4-36)



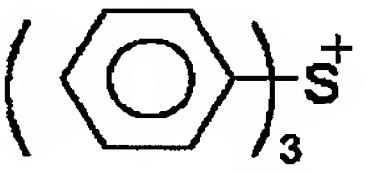
(PAG4-37)



(PAG4-38)



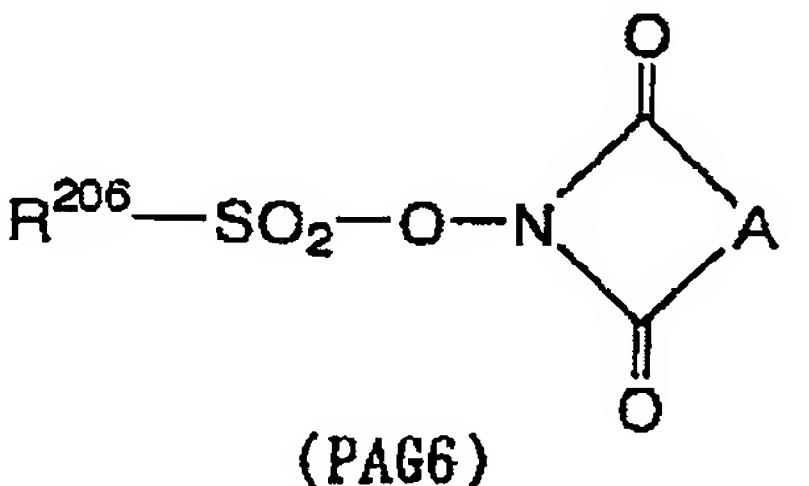
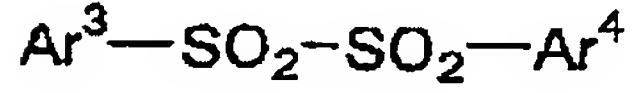
(PAG4-39)



[0081] Moreover, the imino sulfonate derivative expressed with the disulfon derivative or general formula (PAG6) expressed with the following general formula (PAG5) can be mentioned.

[0082]

[Formula 29]



(PAG5)

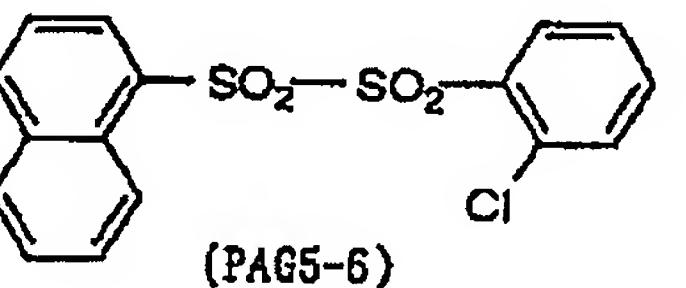
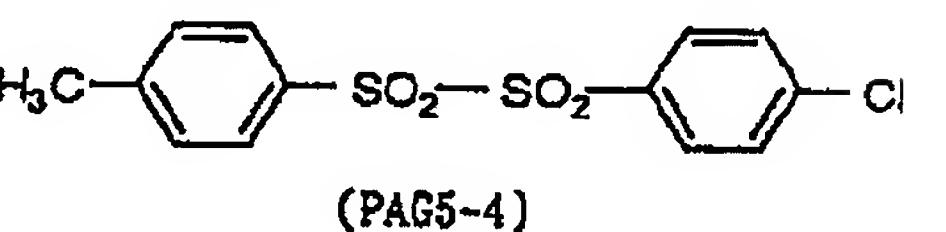
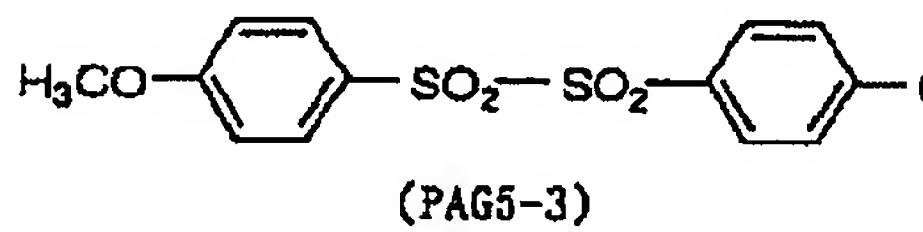
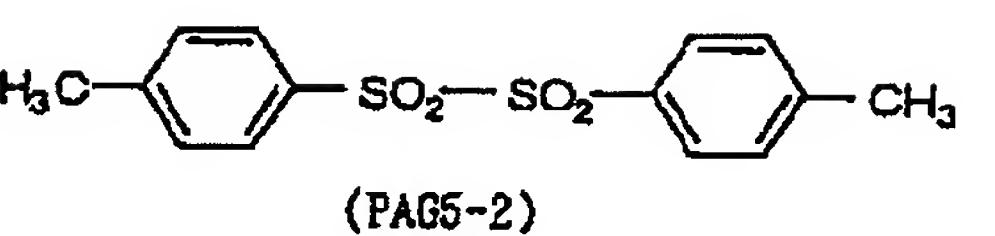
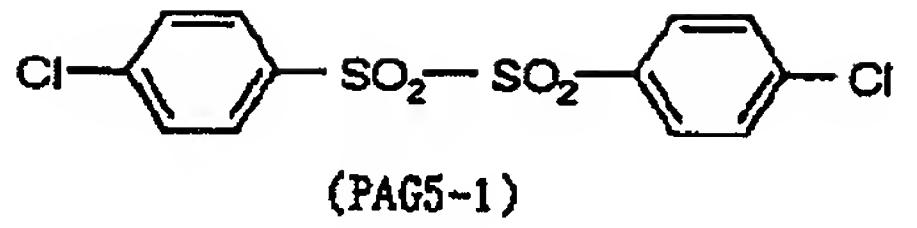
(PAG6)

[0083] Ar3 and Ar4 show respectively the aryl group which is not permuted [a permutation or] independently among a formula. R206 shows the alkyl group which is not permuted [a permutation or] and an aryl group. A shows the alkylene group which is not permuted [a permutation or], an alkenylene group, and an arylene radical.

[0084] Although the compound shown below as an example is mentioned, it is not limited to these.

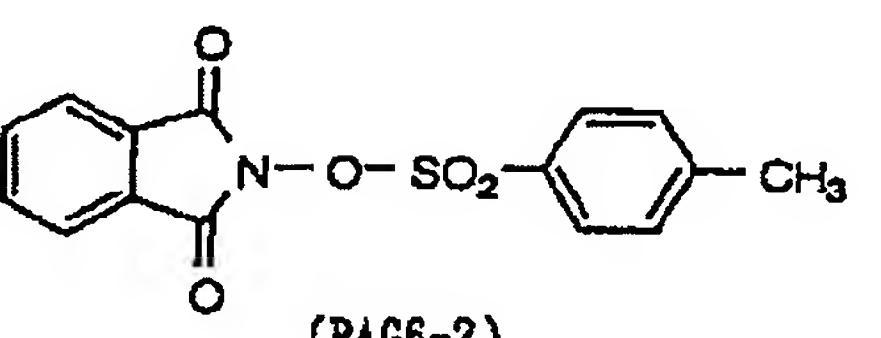
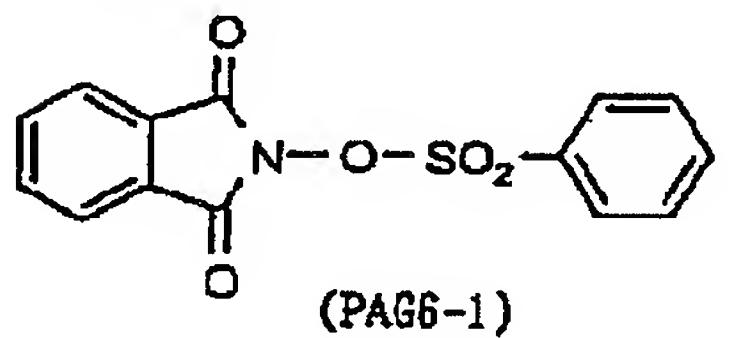
[0085]

[Formula 30]



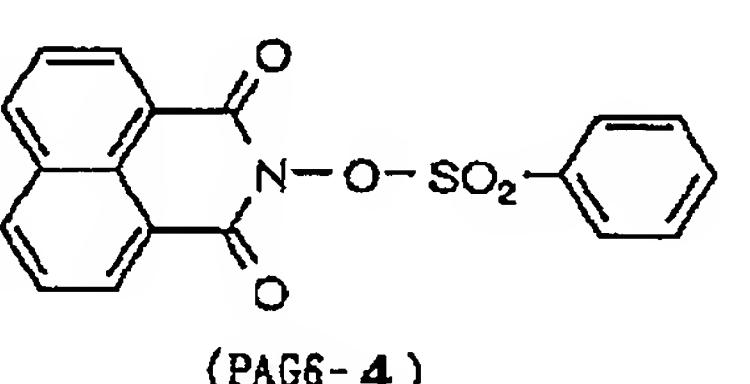
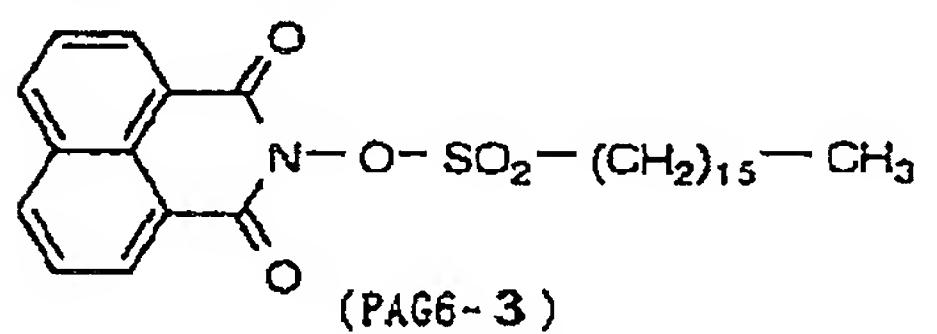
[0086]

[Formula 31]



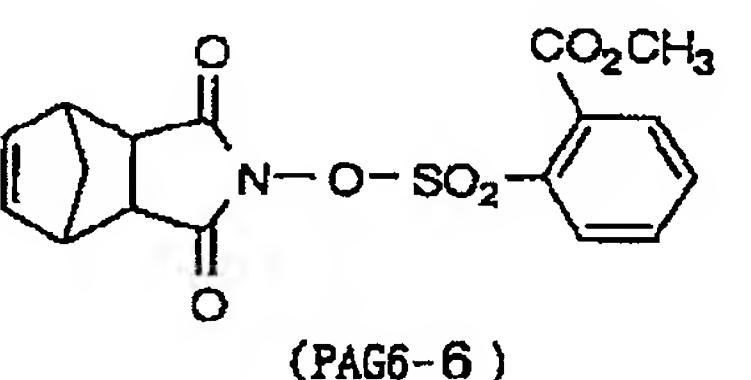
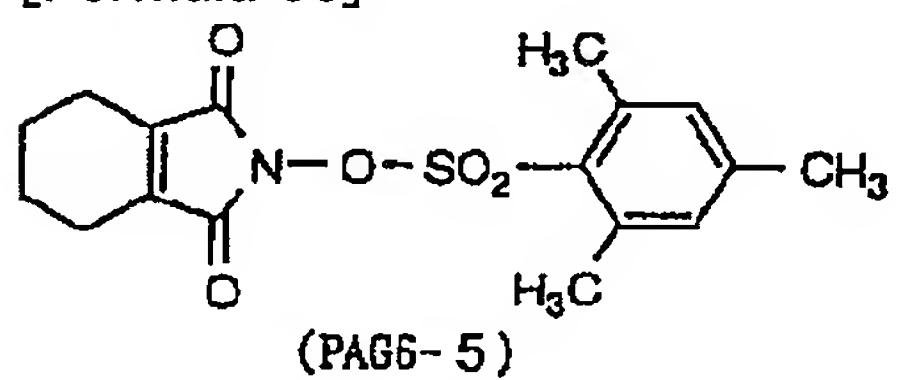
[0087]

[Formula 32]



[0088]

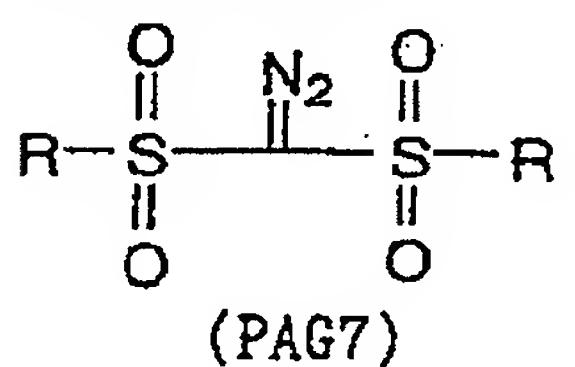
[Formula 33]



[0089] Moreover, the diazo disulfon derivative expressed with the following general formula (PAG7) can be mentioned.

[0090]

[Formula 34]

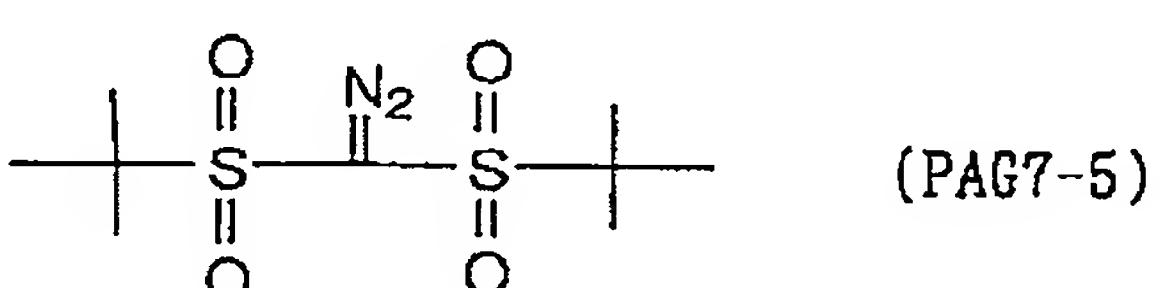
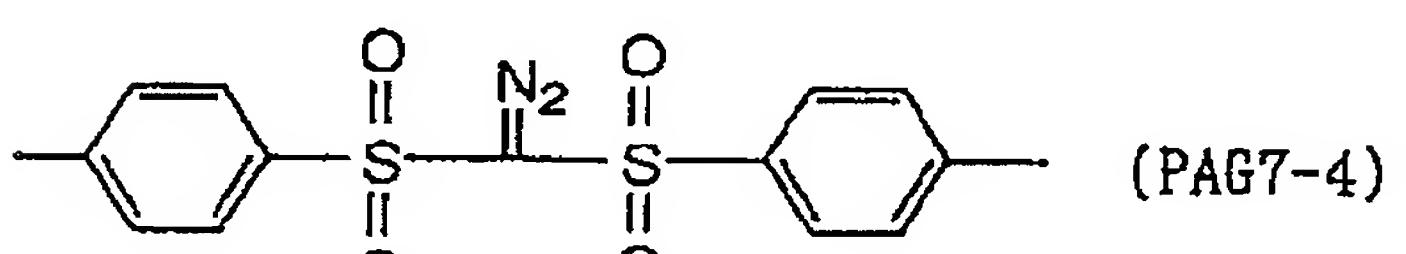
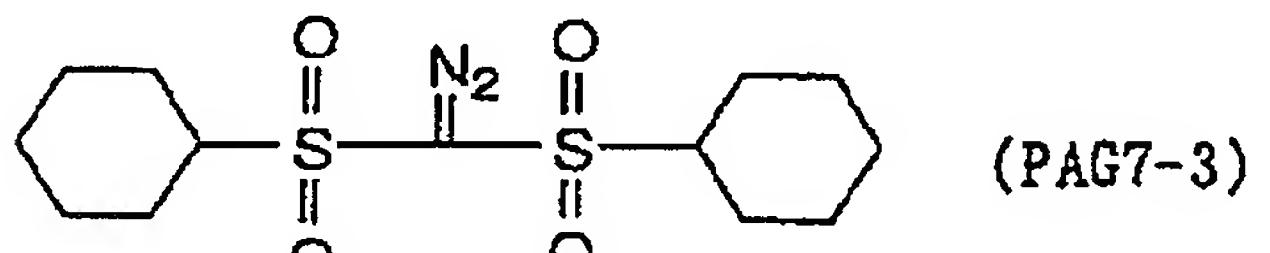
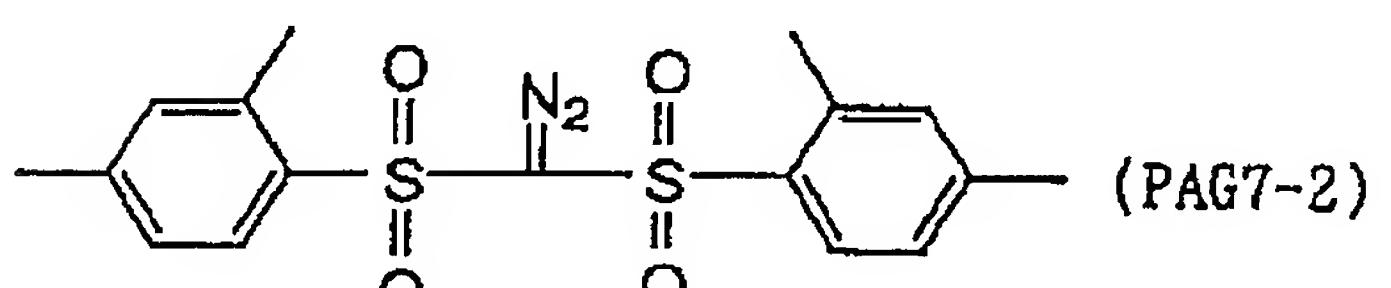
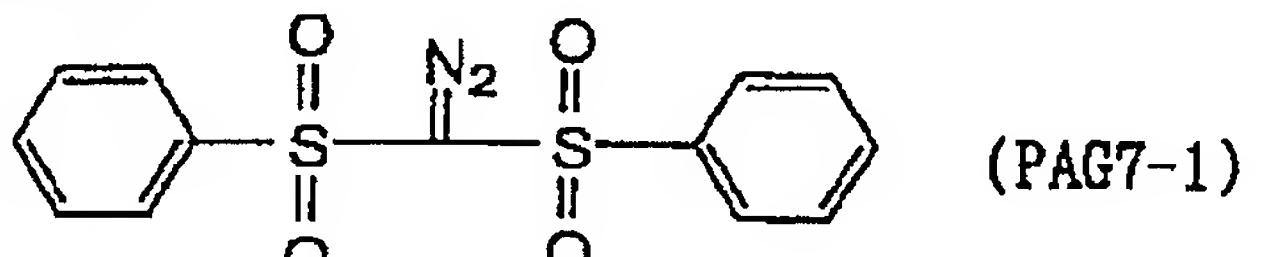


[0091] R expresses among a formula a straight chain, branching, an annular alkyl group, or the aryl group that may be permuted.

[0092] Although the compound shown below as an example is mentioned, it is not limited to these.

[0093]

[Formula 35]



[0094] The compound which reaches the above (A1a) (A1b) can make an aromatic compound able to react using a periodate, and can compound the obtained iodonium salt by carrying out salt exchange to a corresponding sulfonic acid. Moreover, the phenyl sulfoxide which is not permuted [aryl Grignard reagents such as aryl magnesium bromide, a permutation, or] is made to react, and the obtained triarylsulfonium halide can be compounded by the approach of carrying out salt exchange with a corresponding sulfonic acid. Moreover, condensation, the approach of carrying out salt exchange, a diaryl iodonium salt, and a diaryl sulfide are [the phenyl sulfoxide which is not permuted / a permutation or / and a corresponding aromatic compound] compoundable by condensation, the approach of carrying out salt exchange, etc. using catalysts, such as copper acetate, using acid catalysts, such as methansulfonic acid / diphosphorus pentaoxide, or an aluminum chloride. Once leading salt exchange to a halide salt, it can carry out salt exchange also of also using the approach of using silver reagents, such as a silver oxide, and changing into a sulfonate, or ion exchange resin. Moreover, the sulfonic acid or sulfonate used for salt exchange can be obtained by hydrolysis of commercial sulfonic-acid halide etc., using a commercial thing.

[0095] In this invention, it is desirable to use the compound (A2) which decomposes by the exposure of an

activity beam of light or a radiation, and generates a carboxylic acid with the compound (A1) which generates an organic sulfonic acid by the exposure of an activity beam of light or a radiation. The compound (A2a) which decomposes by the exposure of an activity beam of light or a radiation, and generates a fluorine content carboxylic acid as a compound (A2) which decomposes by the exposure of an activity beam of light or a radiation, and generates a carboxylic acid, and the compound (A2b) which decomposes by the exposure of an activity beam of light or a radiation, and generates fluorine a non-containing carboxylic acid can be mentioned.

[0096] (A2a) As a compound fluorine content carboxylic acid which decomposes by the exposure of an activity beam of light or a radiation, and generates a fluorine content carboxylic acid, the aliphatic carboxylic acid by which the fluorine permutation was carried out, and the aromatic carboxylic acid by which the fluorine permutation was carried out can be mentioned.

[0097] As aliphatic carboxylic acid by which the fluorine permutation was carried out, the fluorine permutation object of aliphatic carboxylic acid, such as an acetic acid, a propionic acid, n-butanoic acid, an isobutyric acid, valerianic acid, trimethylacetic acid, a caproic acid, oenanthic acid, a caprylic acid, pelargonic acid, a capric acid, a lauryl acid, a myristic acid, a palmitic acid, stearin acid, undecanoic acid, dodecanoic acid, and a tridecane acid, is mentioned. These may have the hydroxyl group, the alkoxy group, and the halogen atom as a substituent. Moreover, what contains connection radicals, such as an oxygen atom, a sulfur atom, a carbonyl group, a carboxyl group, and a sulfonyl group, in the aliphatic series chain is desirable. What is expressed with the following general formula as desirable aliphatic carboxylic acid by which the fluorine permutation was carried out can be mentioned.

L expresses a hydrogen atom or a fluorine atom among an $L-(CH_2)^p(CF_2)^q(CH_2)^r-COOH$ general formula. p and r express the integer of 0–15, and q expresses the integer of 1–15 independently respectively. The hydrogen atom or fluorine atom of an alkyl chain in this general formula may be permuted by the alkyl group (preferably carbon numbers 1–5) which may be permuted by the fluorine atom, the alkoxy group (preferably carbon numbers 1–5) which may be permuted by the fluorine atom, or the hydroxyl group. It is desirable that the carbon number is the fluorine permutation object of 2–20, and the saturation aliphatic carboxylic acid that is 4–20 more preferably as aliphatic carboxylic acid by which the fluorine permutation was carried out [above-mentioned]. By making this carbon number into four or more pieces, the diffusibility of the carboxylic-acid resolvability to generate falls and the line breadth change by the passage of time from exposure to afterbaking can be controlled more. Especially, the fluorine permutation object of the straight chain of 4–18 carbon numbers or branching saturation aliphatic carboxylic acid is desirable.

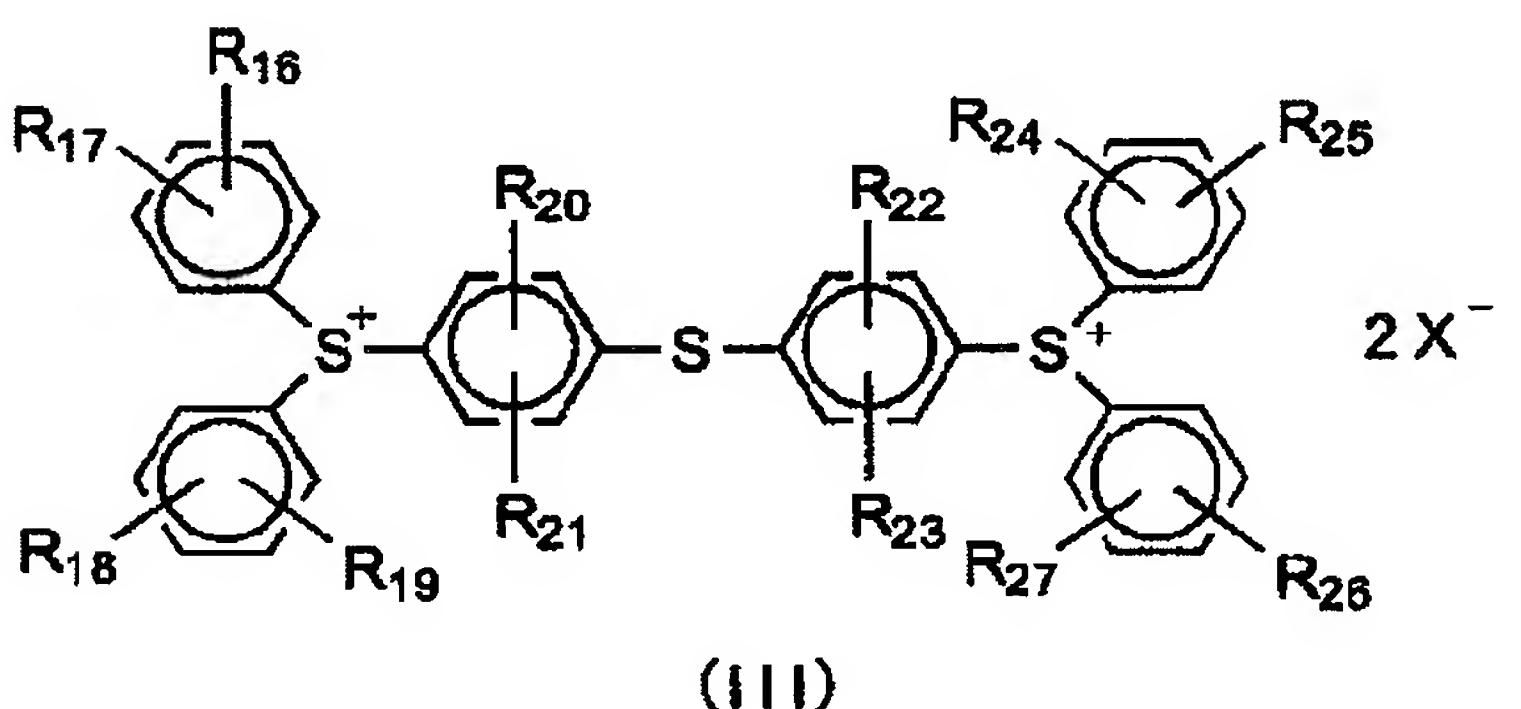
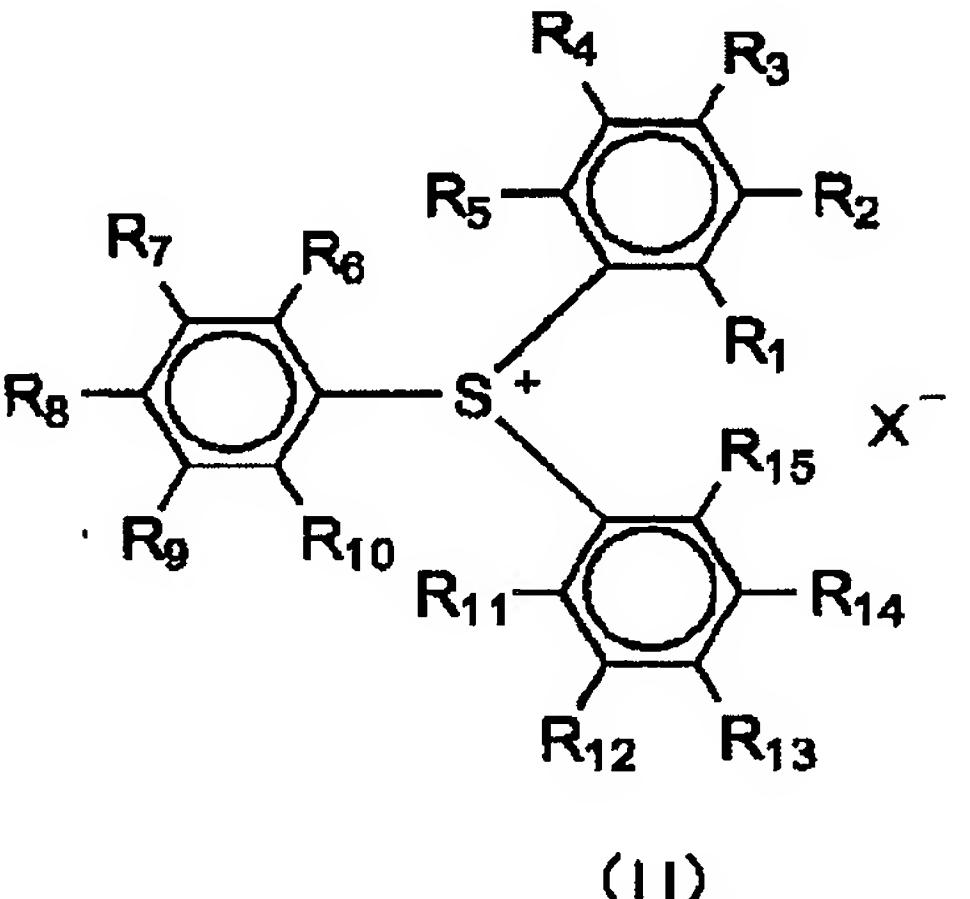
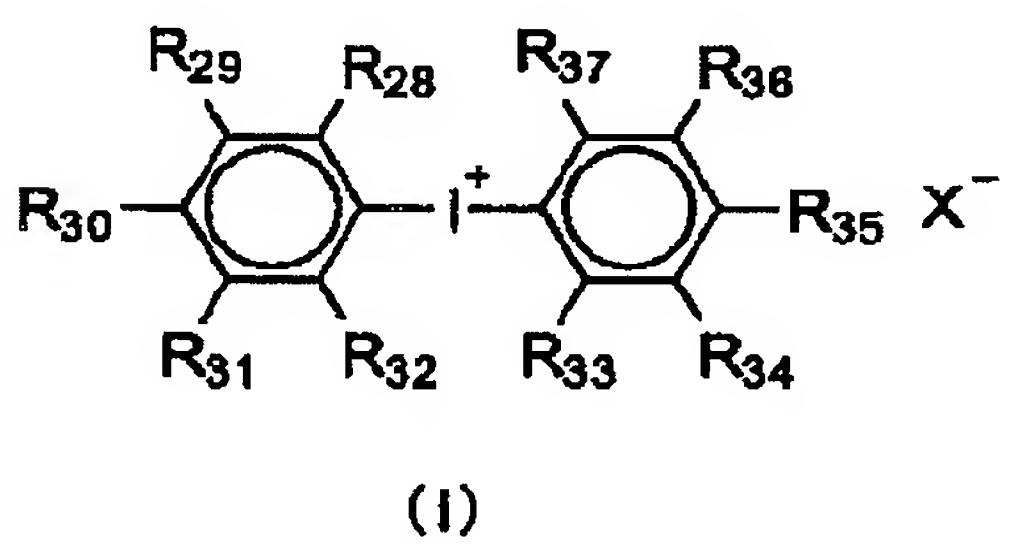
[0098] As an aromatic series group carboxylic acid by which the fluorine permutation was carried out, it is desirable that carbon numbers are 7–20, and the fluorine permutation object of the aromatic carboxylic acid which is 7–15 more preferably and is 7–11 still more preferably. Specifically, the fluorine permutation object of aromatic carboxylic acid, such as a benzoic acid, a permutation benzoic acid, a naphthoic acid, a permutation naphthoic acid, an anthracene carboxylic acid, and a permutation anthracene carboxylic acid (it is here and an alkyl group, an alkoxy group, a hydroxyl group, a halogen atom, an aryl group, an acyl group, an acyloxy radical, a nitro group, an alkylthio group, and an aryl thio radical are mentioned as a substituent), is mentioned. Especially, the fluorine permutation object of a benzoic acid and a permutation benzoic acid is desirable.

[0099] The carboxylic acid of the aliphatic series permuted by these fluorines atom or aromatic series is a carboxylic acid (perfluoro saturation aliphatic carboxylic acid or perfluoro aromatic carboxylic acid) of the aliphatic series by which one or more of the hydrogen atom which exists in frames other than a carboxyl group were permuted by the fluorine atom, and all the hydrogen atoms that exist in frames other than a carboxyl group preferably especially were permuted by the fluorine atom, or aromatic series. Thereby, sensibility comes to be further excellent. In addition, especially about an aliphatic-carboxylic-acid anion, the anion which has a fluorine atom on alpha carbon atom of a carboxylic acid has high acid strength, and is in the inclination to perform salt exchange easily to the carboxylic-acid anion which does not have a fluorine atom. Moreover, perfluoro aliphatic carboxylic acid has still higher acid strength.

[0100] The onium salt compounds (sulfonium salt, iodonium salt, etc.) which have the anion of the carboxylic acid of the aliphatic series permuted by the above fluorine atoms or aromatic series as a counter anion as a compound which decomposes by the exposure of an activity beam of light or a radiation, and generates a fluorine content carboxylic acid, the imide carboxylate compound which has a carboxylate radical, or a nitrobenzyl ester compound is mentioned. The compound more preferably expressed with the following general formula (I) – (III) is mentioned. Thereby, sensibility, resolving power, and an exposure margin come to be further excellent. This compound generates the carboxylic acid of the saturation aliphatic series permuted by at least one fluorine atom which decomposes by the exposure of an activity beam of light or a radiation, and is equivalent to X^- of a general formula (I) – (III), or aromatic series.

[0101]

[Formula 36]



[0102] (R1 –R37 express a hydrogen atom, a straight chain, branching or an annular alkyl group, a straight chain, branching or an annular alkoxy group, a hydroxy group, a halogen atom, or 38 –S–R independently respectively among the above-mentioned formula.) R38 expresses a straight chain, branching, an annular alkyl group, or an aryl group here. X[–] is the anion of the carboxylic acid of the aliphatic series permuted by at least one fluorine atom, or aromatic series.

X[–] is the anion of perfluoro aliphatic carboxylic acid or perfluoro aromatic carboxylic acid preferably, and is the anion of the fluorine permutation alkyl carboxylic acid of four or more carbon numbers especially preferably.

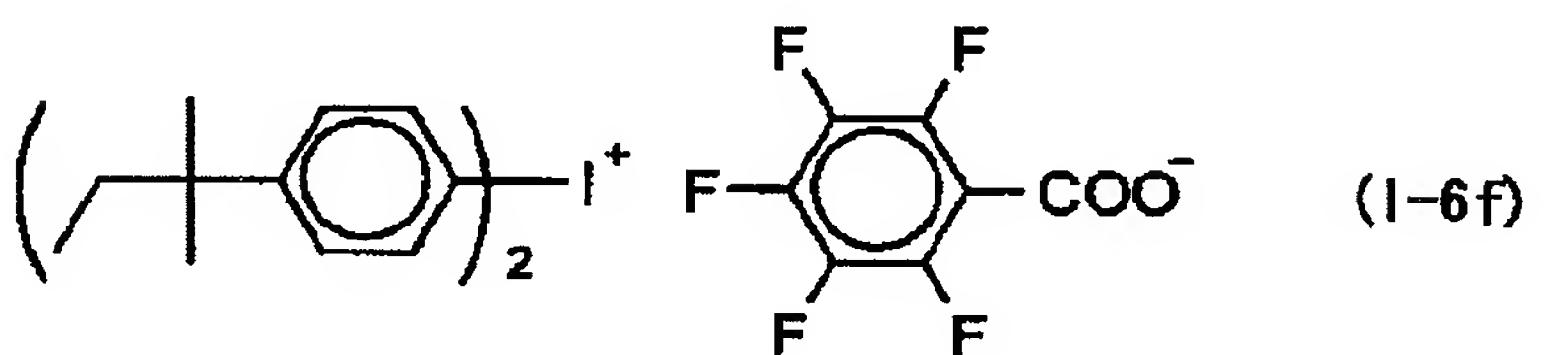
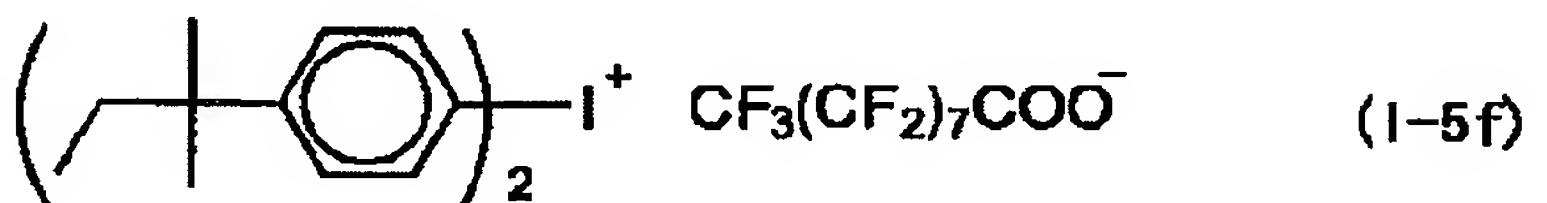
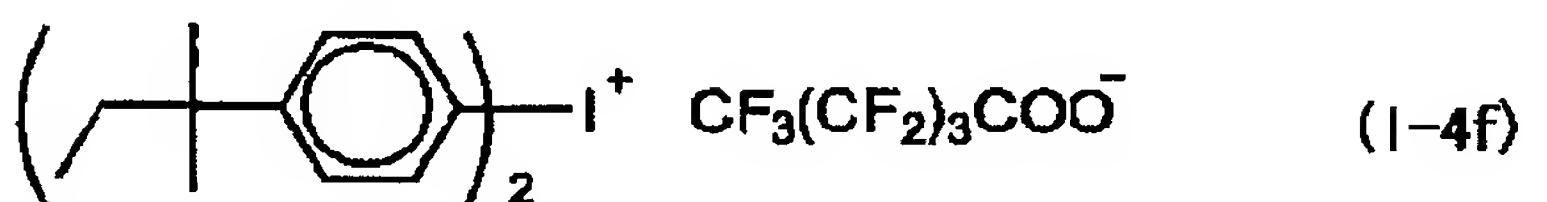
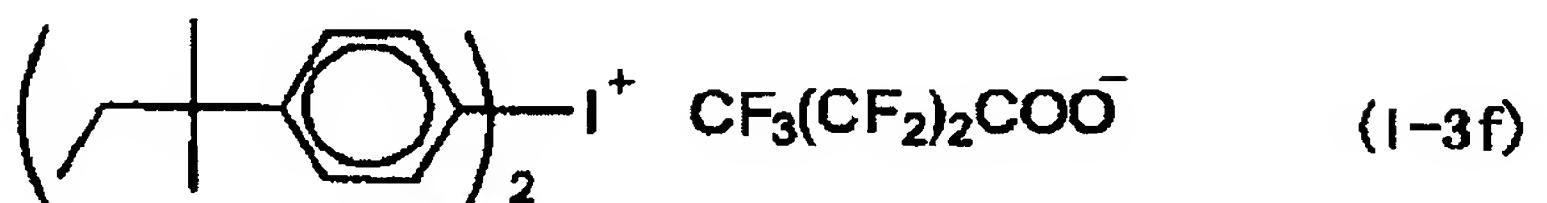
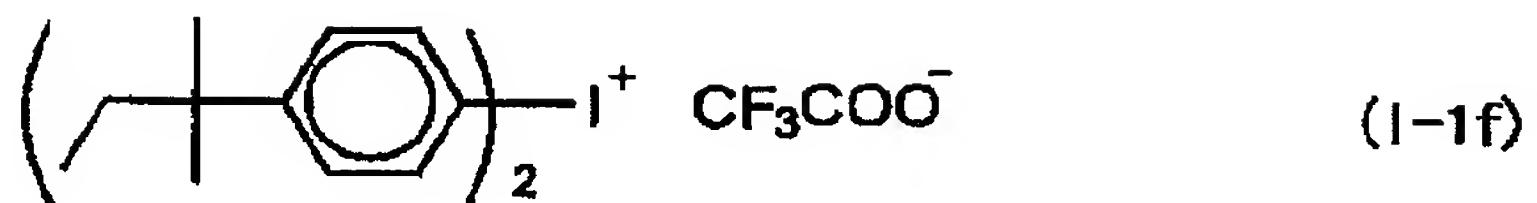
[0103] The thing of 1–4 carbon numbers like a methyl group, an ethyl group, a propyl group, n–butyl, sec–butyl, and t–butyl in a general formula (I) – (III) which may have a substituent as the straight chain of R1–R38 and a branching alkyl group is mentioned. As an annular alkyl group, the thing of 3–8 carbon numbers like a cyclo propyl group, a cyclopentyl group, and a cyclohexyl radical which may have a substituent is mentioned. As an alkoxy group of R1–R37, the thing of 1–4 carbon numbers like a methoxy group, an ethoxy radical, a hydroxy ethoxy radical, a propoxy group, an n–butoxy radical, an iso butoxy radical, a sec–butoxy radical, and a t–butoxy radical is mentioned. As a halogen atom of R1–R37, a fluorine atom, a chlorine atom, a bromine atom, and iodine atom can be mentioned. As an aryl group of R38, the thing of 6–14 carbon numbers, such as a phenyl group, a tolyl group, a methoxyphenyl radical, and a naphthyl group, is mentioned. An aryl group may have a substituent. The alkoxy group of 1–4 carbon numbers, a halogen atom (a fluorine atom, a chlorine atom, iodine atom), the aryl group of 6–10 carbon numbers, the alkenyl radical of 2–6 carbon numbers, a cyano group, a hydroxy group, a carboxy group, an alkoxy carbonyl group, a nitro group, etc. are mentioned preferably as these substituents.

[0104] The iodonium compound or sulfonium compound expressed with the general formula (I) used by this invention – (III) has the anion of the carboxylic acid of the saturation aliphatic series permuted by at least one fluorine atom, or aromatic series as the Xfor anion[–]. These anions are anions (–COO[–]) from which the hydrogen atom of this carboxylic acid (–COOH) seceded.

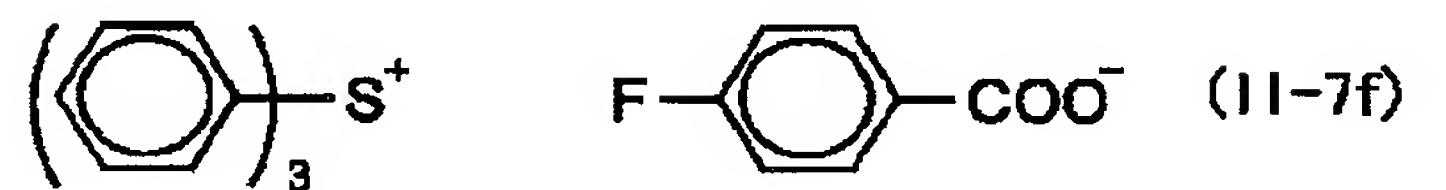
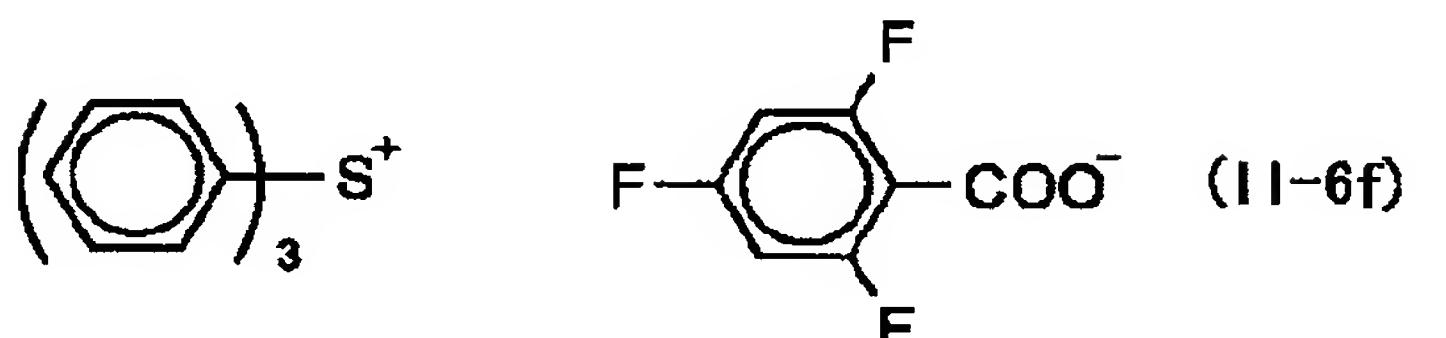
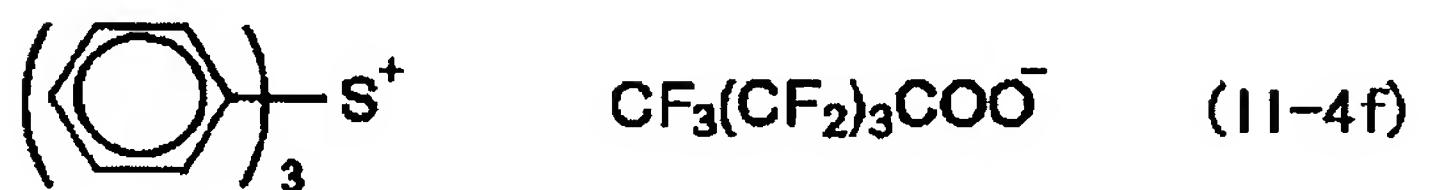
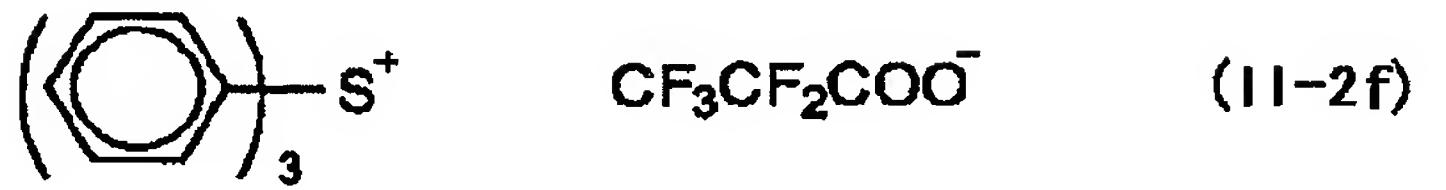
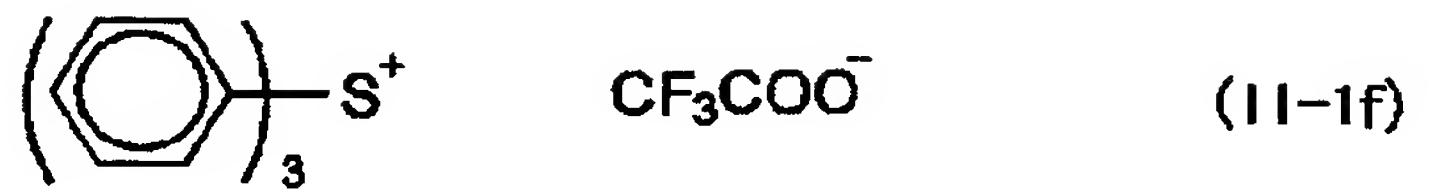
[0105] Although an example is shown below, this invention is not limited to these.

Example of a compound expressed with a general formula (I) : [0106]

[Formula 37]

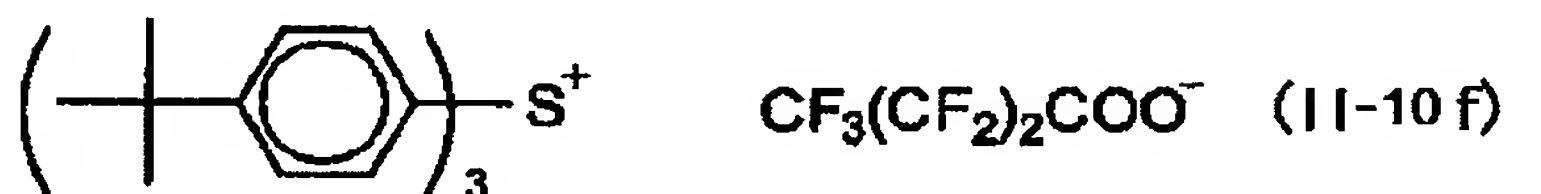
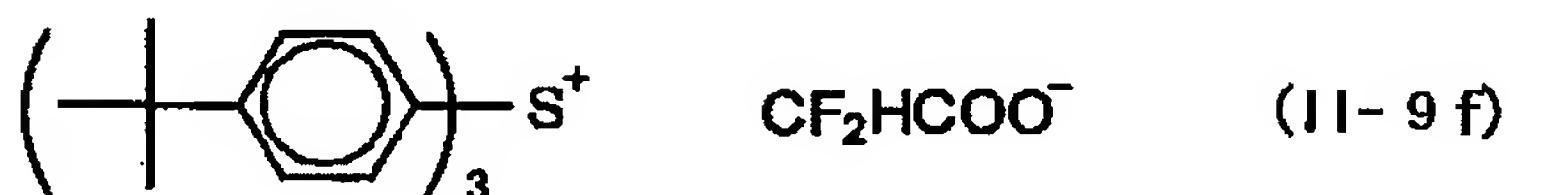
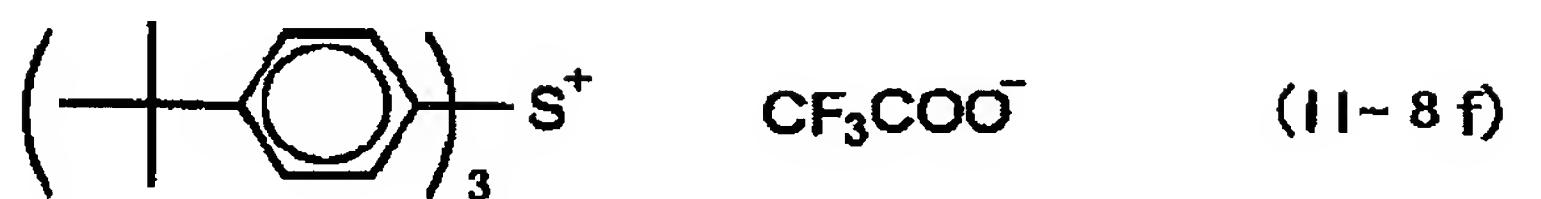


[0107] The example of a compound expressed with a general formula (II): [Formula 38]



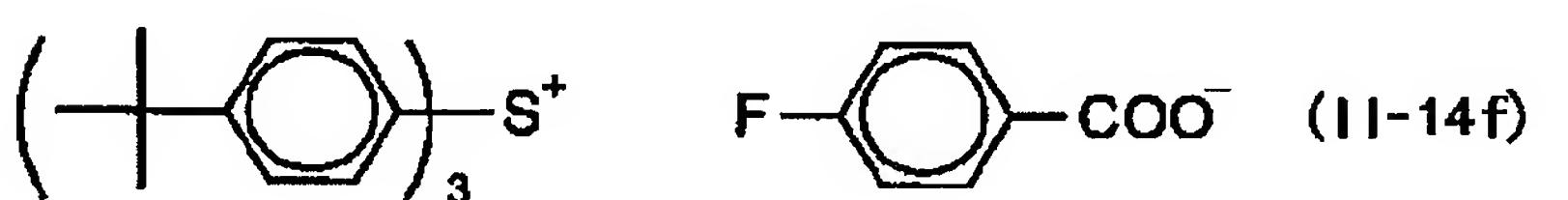
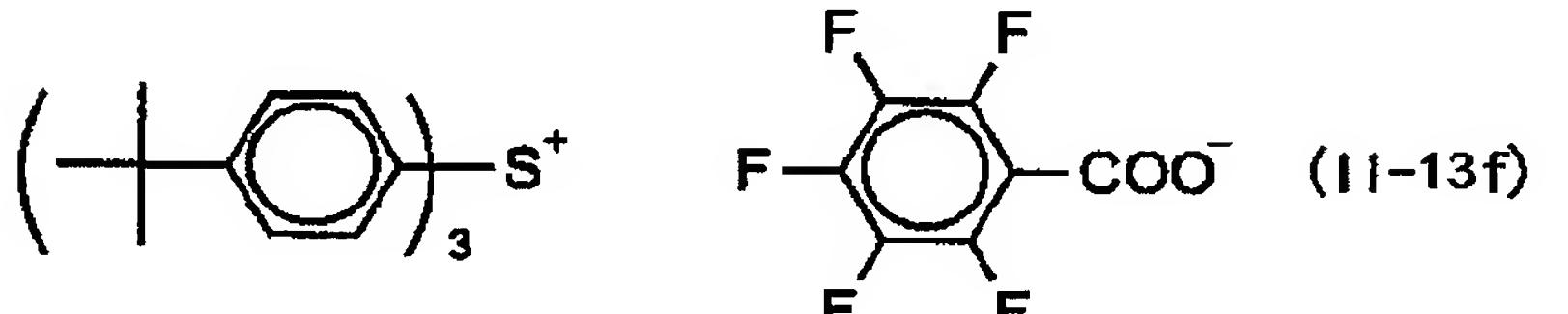
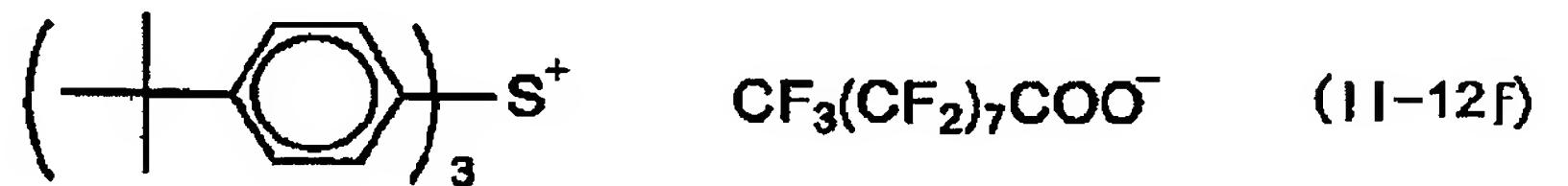
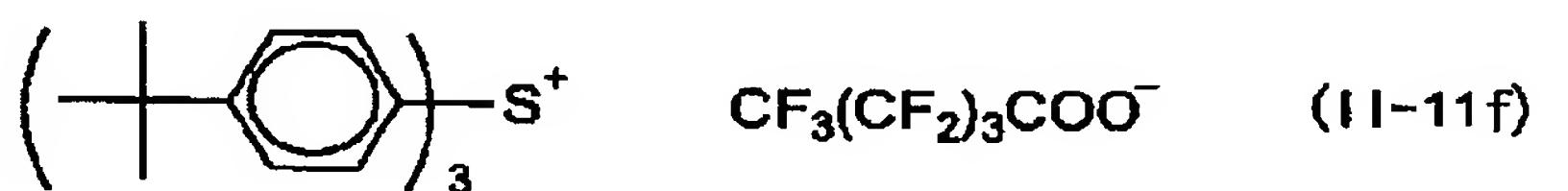
[0108]

[Formula 39]



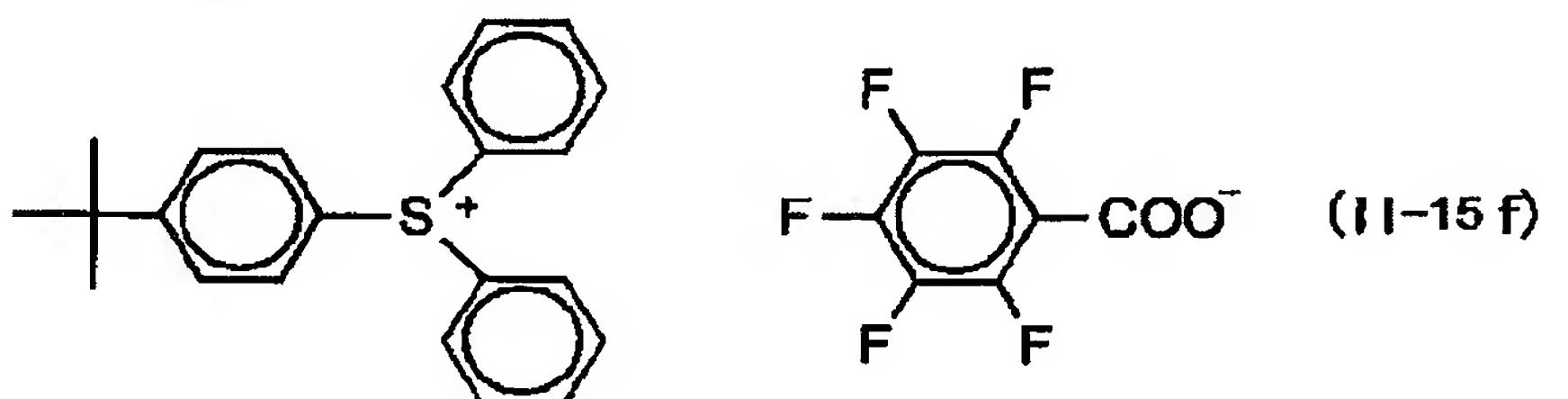
[0109]

[Formula 40]



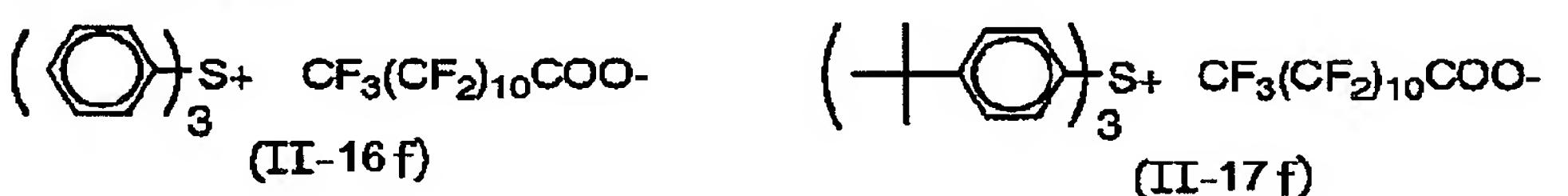
[0110]

[Formula 41]



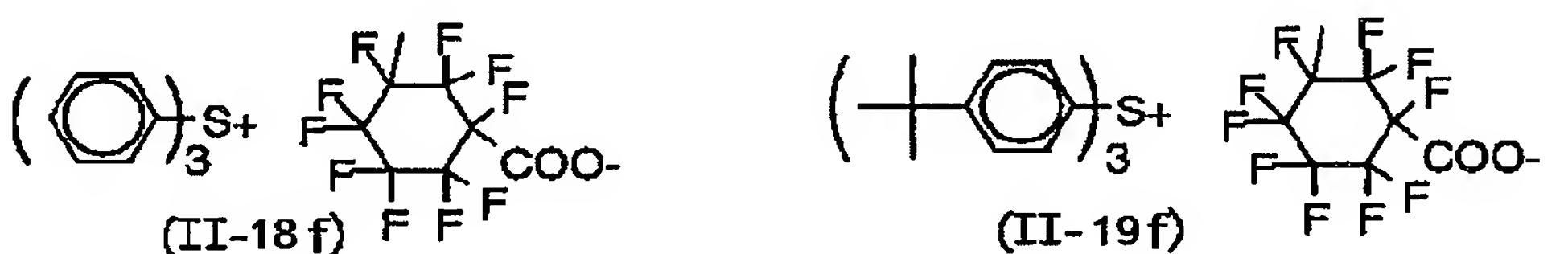
[0111]

[Formula 42]



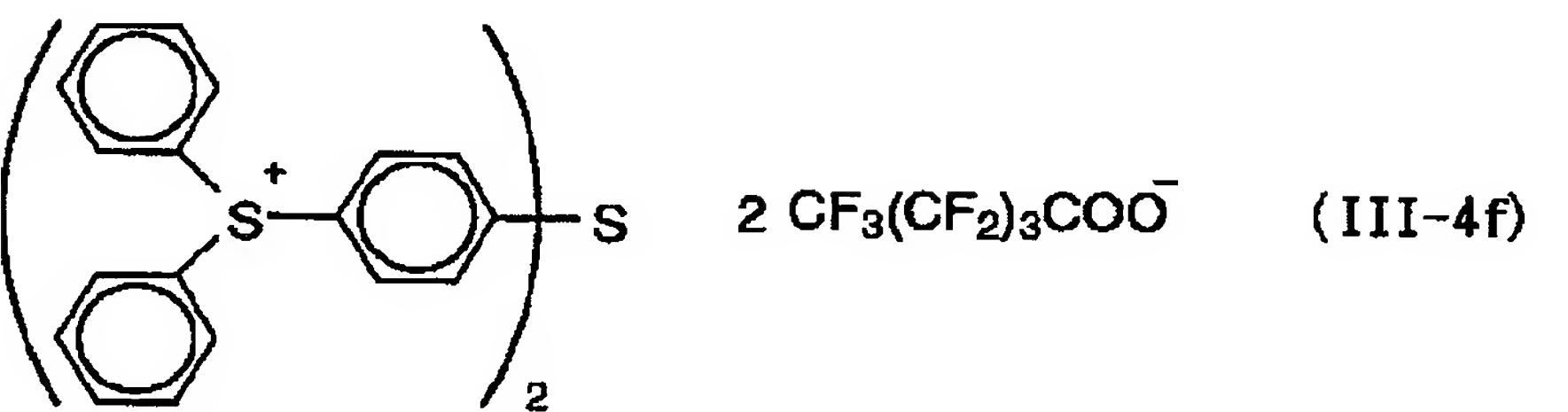
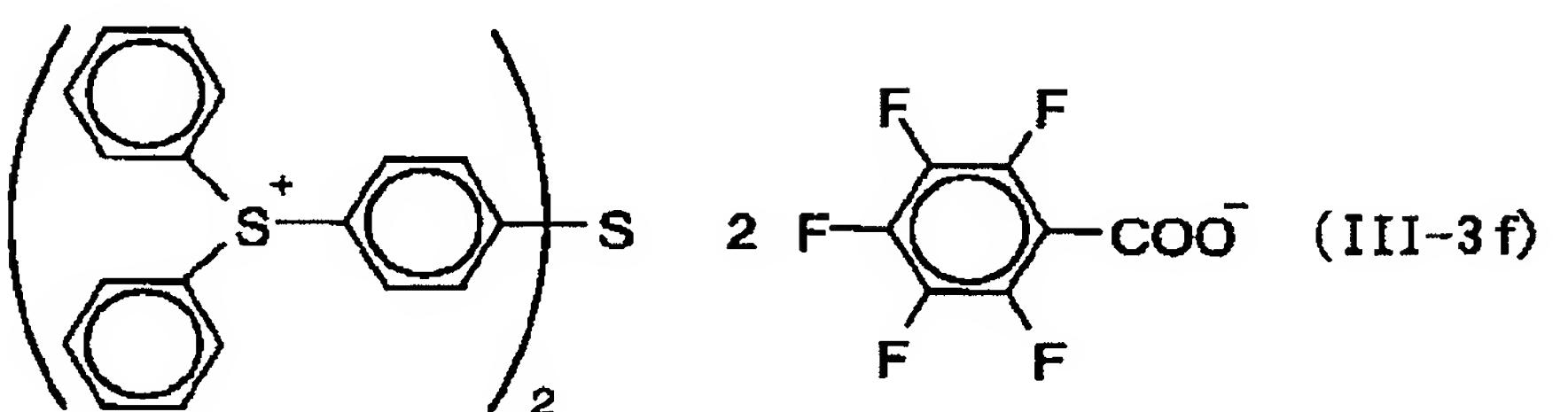
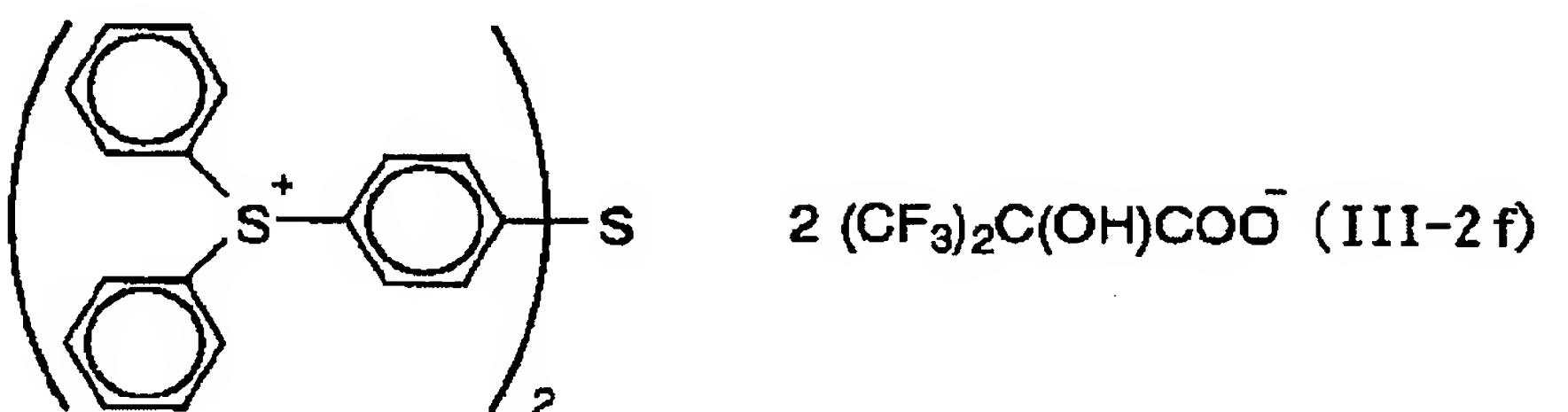
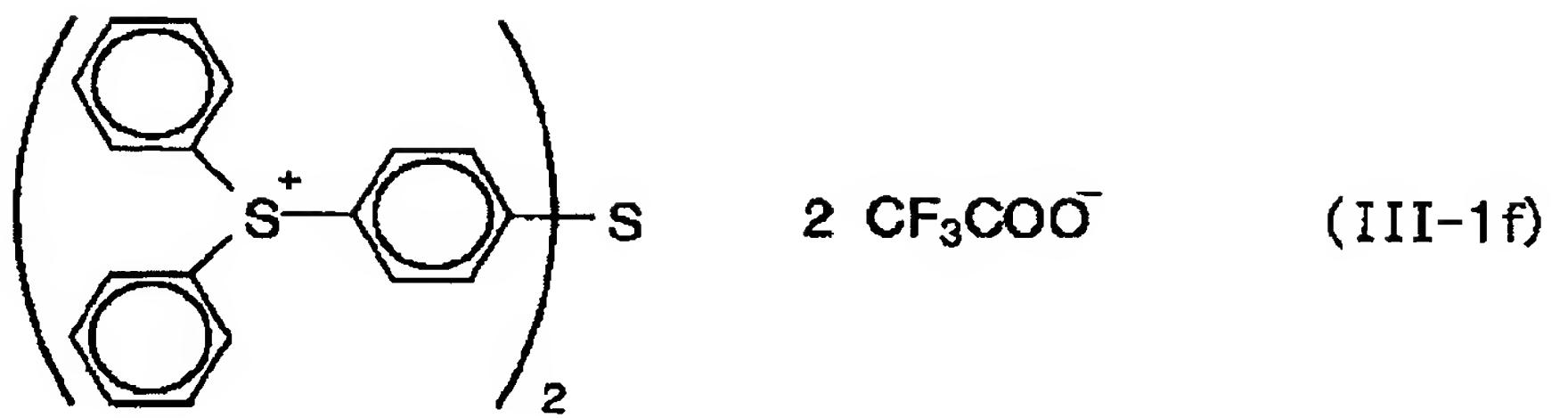
[0112]

[Formula 43]



[0113] Example of a compound expressed with a general formula (III) : [0114]

[Formula 44]



[0115] Example of other compounds : [0116]

[Formula 45]

[0117] The compound expressed with the above-mentioned general formula (I) can make an aromatic compound able to react using a periodate, and can compound the obtained iodonium salt by carrying out salt exchange to a corresponding carboxylic acid. The compound expressed with a general formula (II) and a general formula (III) makes the phenyl sulfoxide which is not permuted [aryl Grignard reagents, such as for example, aryl magnesium bromide, a permutation, or] react, and can compound the obtained triarylsulfonium halide by the approach of carrying out salt exchange with a corresponding carboxylic acid. Moreover, condensation, the approach of carrying out salt exchange, a diaryl iodonium salt, and a diaryl sulfide are [the phenyl sulfoxide which is not permuted / a permutation or / and a corresponding aromatic compound] compoundable by condensation, the approach of carrying out salt exchange, etc. using catalysts, such as copper acetate, using acid catalysts, such as methansulfonic acid / diphosphorus pentaoxide, or an aluminum chloride. Once leading salt exchange to a halide salt, it can carry out salt exchange also of also

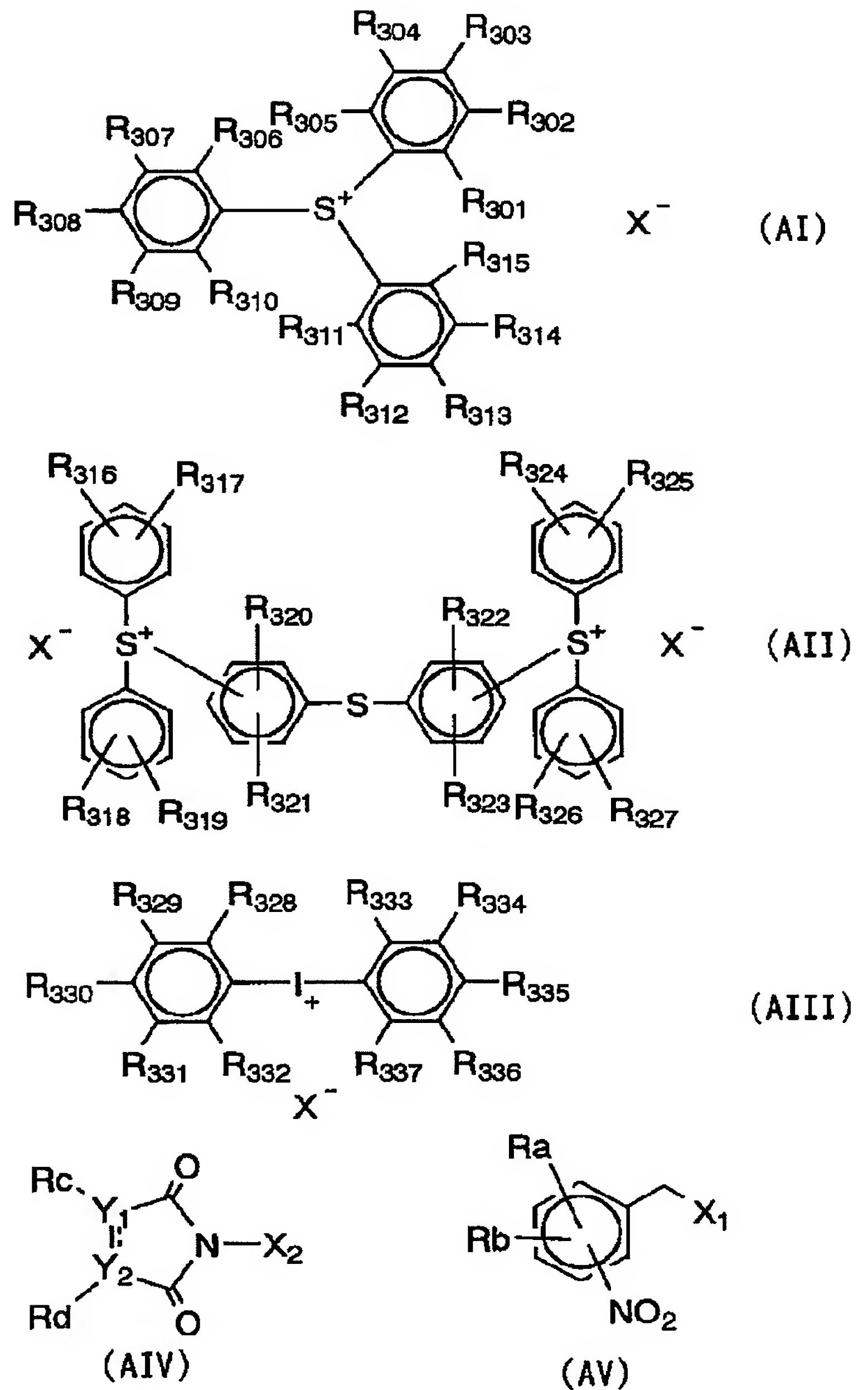
using the approach of using silver reagents, such as silver oxide, and changing into carboxylate, or ion exchange resin. Moreover, the carboxylic acid or carboxylate used for salt exchange can be obtained by hydrolysis of commercial carboxylic-acid halide etc., using a commercial thing.

[0118] The thing using what is drawn from the fluoro aliphatic compound manufactured by the telomerization method (called the telomer method) or the co-oligomerization method (called the oligomer method) of the carboxylic acid by which the fluorine permutation was carried out as an anion part is also desirable. The manufacturing method of these fluoro aliphatic compounds is indicated by 117–118 pages of "composition of a fluorine compound, and a function" (editorial supervision: Nobuo Ishikawa, issue:CMC Co., Ltd., 1987), and 747 – 752 pages of "Chemistry of Organic Fluorine Compounds II" (Monograph 187, Ed by Milos Hudlicky and Attila E. Pavlath, and American Chemical Society 1995), for example. The telomerization method is the approach of performing the radical polymerization of fluorine content vinyl compounds, such as tetrafluoroethylene, by making the large alkyl halide of chain transfer constants, such as an iodide, into TEROGEN, and compounding a telomer (the example was shown in Scheme-1). Although the mixture of two or more compounds with which chain length differs in composition by the telomer method is obtained, it may be used with mixture, and it may refine and this may be used.

[0119] (A2b) As a compound which decomposes by the exposure of the compound activity beam of light or radiation which decomposes by the exposure of an activity beam of light or a radiation, and generates fluorine a non-containing carboxylic acid, and generates fluorine a non-containing carboxylic acid, the compound shown by the following general formula (AI) – (AV) can be mentioned, for example.

[0120]

[Formula 46]

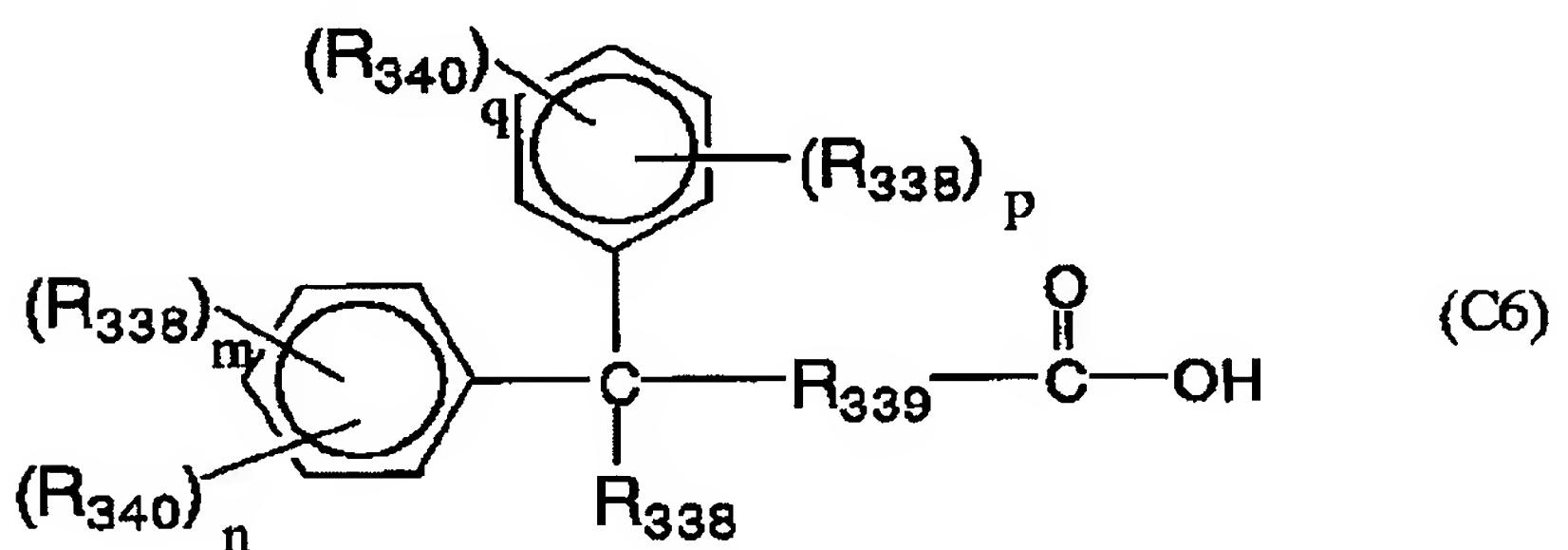
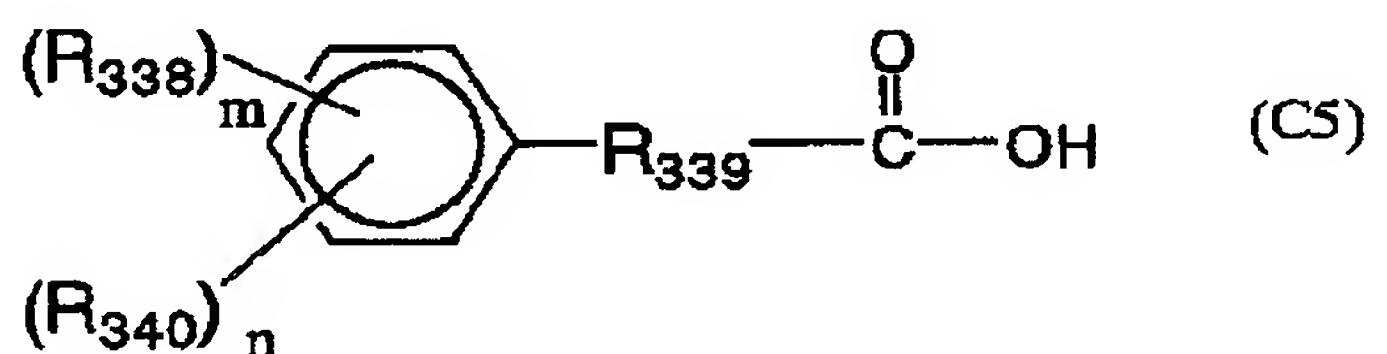
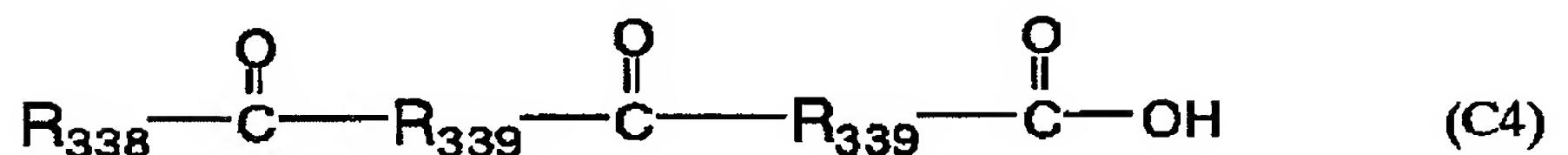
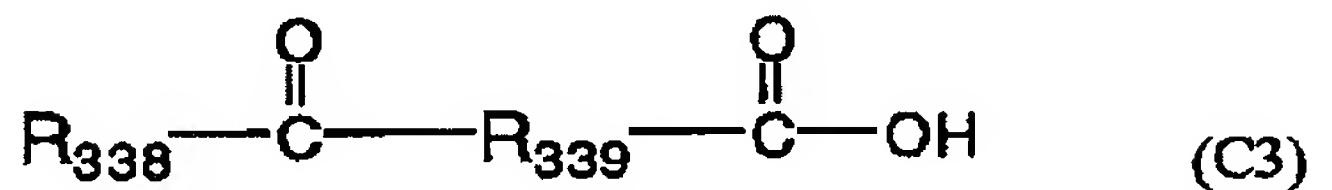
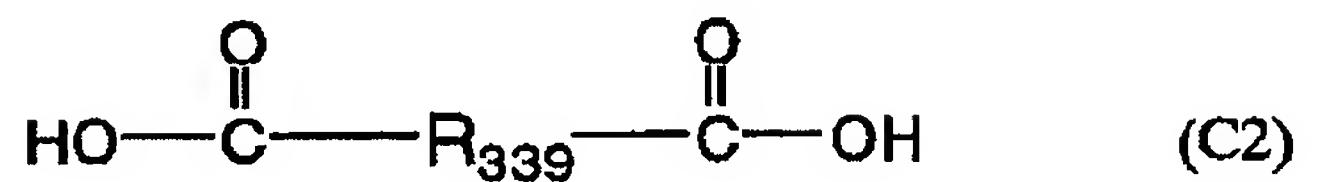
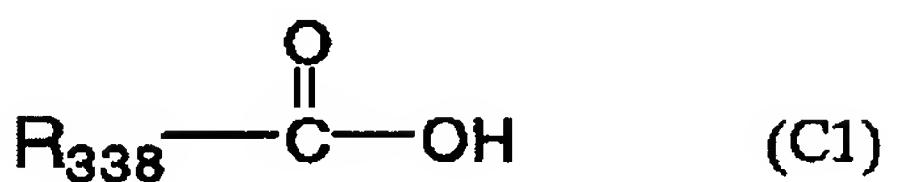


[0121] In the above-mentioned formula, $R_{301} - R_{337}$ express a hydrogen atom, a straight chain, branching or an annular alkyl group, a straight chain, branching or an annular alkoxy group, a hydroxy group, a halogen atom, or zero $-S-R$ independently respectively. R_0 expresses a straight chain, branching, an annular alkyl group, or an aryl group. R_a and R_b express the alkyl group and alkoxy group which may have the hydrogen atom, the nitro group, the halogen atom, and the substituent independently respectively. R_c and R_d express the alkyl group or aryl group which may have the halogen atom and the substituent independently respectively. R_c and R_d may join together and the cyclic hydrocarbon (the oxygen atom and the nitrogen atom may be included in endocyclic [these]) of a ring, a monocycle, or many rings may be formed. Y_1 and Y_2 may express a carbon atom, and single bond or double association is sufficient as Y_1-Y_2 association. Above-mentioned X^- expresses that from which the carboxylic-acid compound shown by the following formula became an anion. X_1 and X_2 express respectively that from which the carboxylic-acid compound

shown by the following formula became an ester group in the carboxyl group part independently.

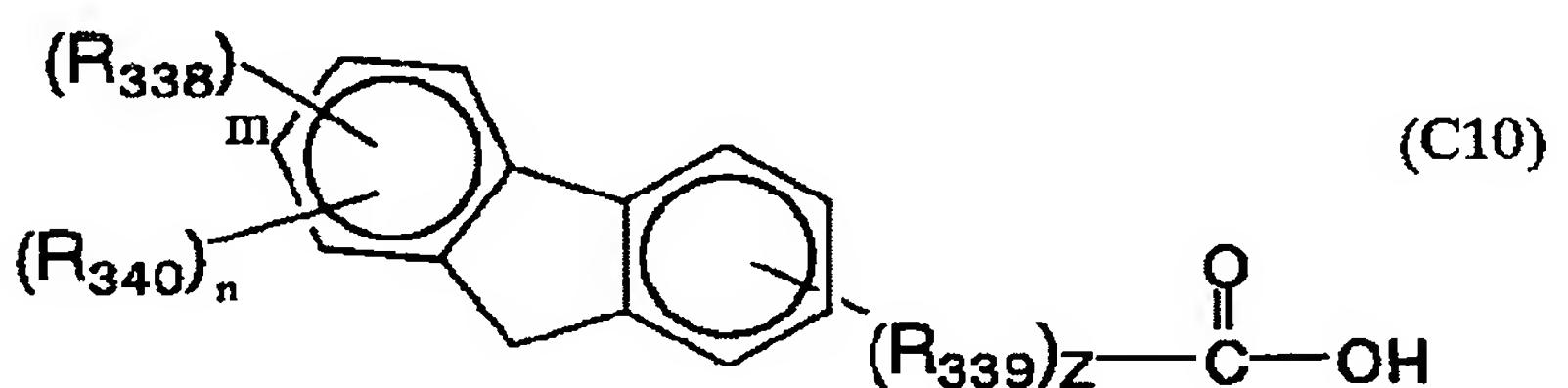
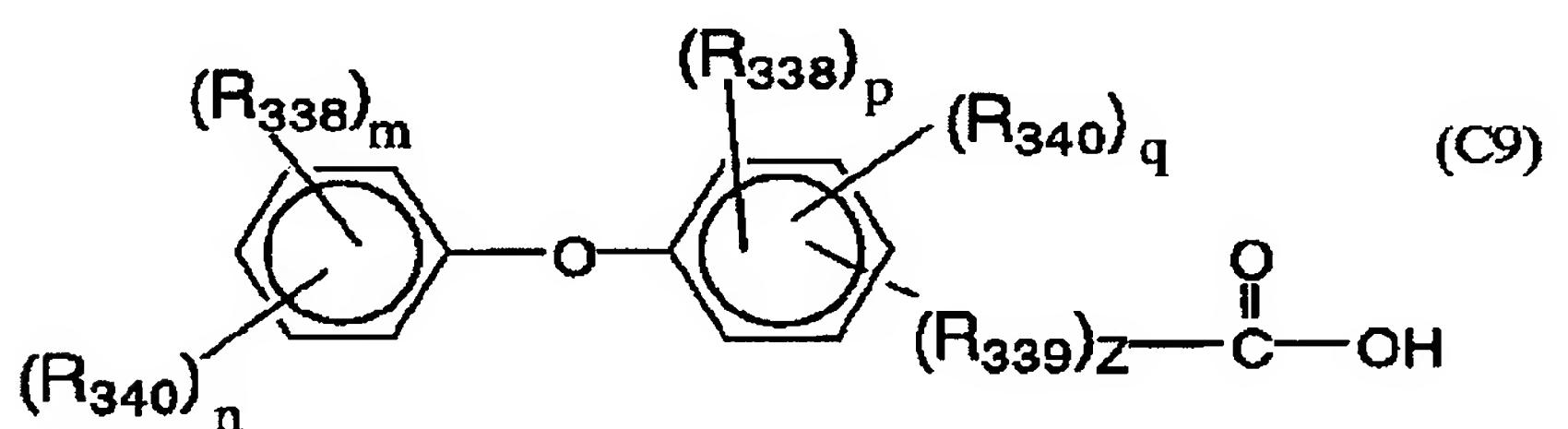
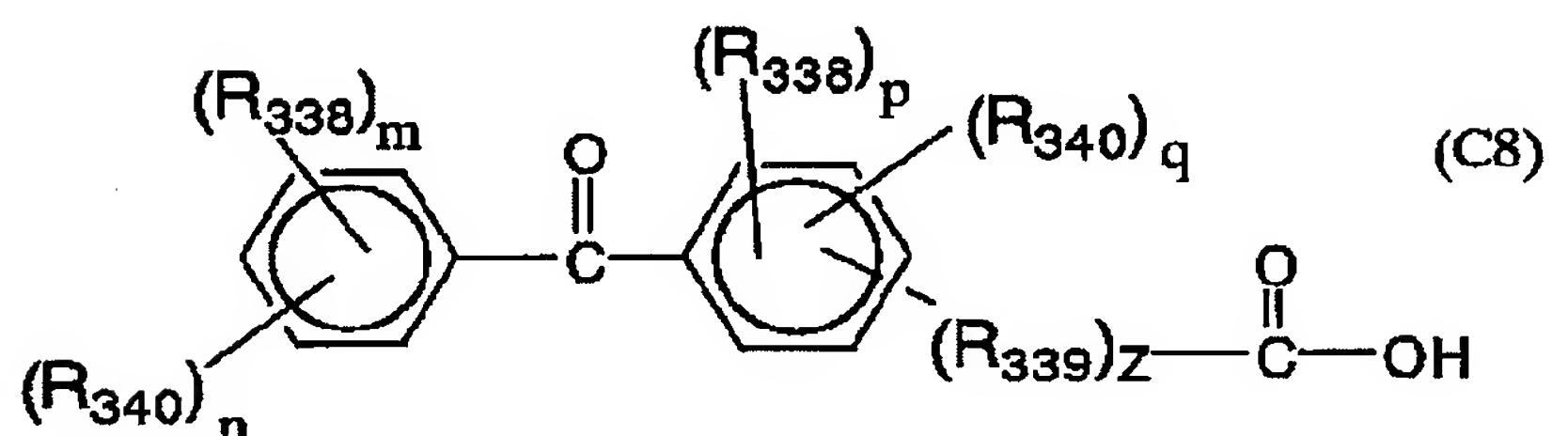
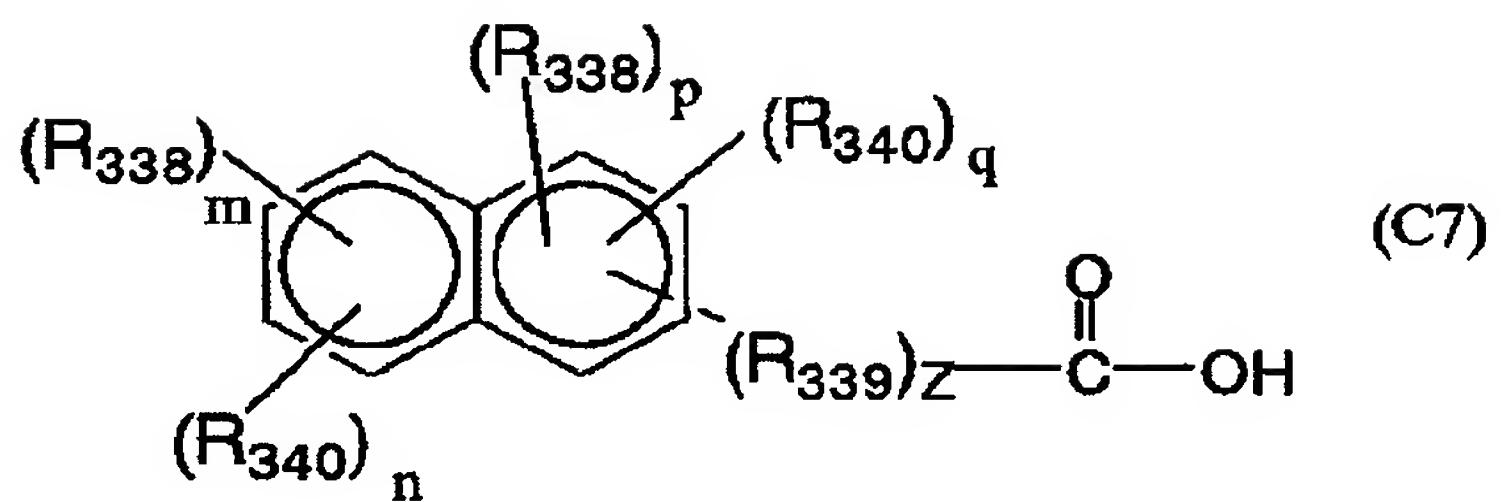
[0122]

[Formula 47]



[0123]

[Formula 48]



[0124] The inside of the above-mentioned formula and R338 are the shape of a straight chain, the letter of branching, or the annular alkyl group (it is here) of carbon numbers 1-30. Even if the oxygen atom and the nitrogen atom are included in the chain of an alkyl group, the shape of a good straight chain of carbon numbers 1-20, The shape of the letter of branching or an annular alkenyl radical, and a straight chain of carbon numbers 1-20, the letter of branching, or an annular alkynyl group, The shape of a straight chain of carbon numbers 1-20, the letter of branching or an annular alkoxyl group, the radical by which a part of hydrogen atom [at least] of said alkyl group was permuted with the halogen atom and/or the hydroxyl group, The permutation or the unsubstituted aryl group of the radical by which a part of hydrogen atom [at least] of said alkenyl radical was permuted with the halogen atom and/or the hydroxyl group, or carbon numbers 6-20 is shown. Here, as a substituent of an aryl group, an alkyl group, a nitro group, a hydroxyl group, an alkoxy group, an acyl group, an alkoxy carbonyl group, and a halogen atom can be mentioned.

[0125] R339 is the shape of single bond or a straight chain of carbon numbers 1-20, a letter of branching, or an annular alkylene group (it is here). Even if the oxygen atom and the nitrogen atom are included in the

chain of an alkylene group, the shape of a good straight chain of carbon numbers 1–20, The letter of branching or an annular alkenylene group, the radical by which a part of hydrogen atom [at least] of said alkylene group was permuted with the halogen atom and/or the hydroxyl group, The radical by which a part of hydrogen atom [at least] of said alkenylene group was permuted by the halogen atom, or the ARUKOKI alkylene group of carbon numbers 2–20 is shown, R338 and R339 existing [two or more] may be the same to mutual, or they may differ in it.

[0126] R340 shows a hydroxyl group or a halogen atom, and R340 existing [two or more] may be the same to mutual, or may differ in it. Respectively, independently, m, n, p, and q are the integers of 0–3, and are $m+n \leq 5$ and $p+q \leq 5$. z is 0 or 1.

[0127] The thing of 1–4 carbon numbers like a methyl group, an ethyl group, a propyl group, n–butyl, sec–butyl, and t–butyl in said general formula (AI) – (AV) which may have a substituent as R301–R337, the straight chain in Ra, Rb, Rc, Rd, and R0, and a branching alkyl group is mentioned. As an annular alkyl group, the thing of 3–8 carbon numbers like a cyclo propyl group, a cyclopentylic group, and a cyclohexyl radical which may have a substituent is mentioned. As an alkoxy group of R301–R337, and Ra and Rb, the thing of 1–4 carbon numbers like a methoxy group, an ethoxy radical, a hydroxy ethoxy radical, a propoxy group, an n–butoxy radical, an iso butoxy radical, a sec–butoxy radical, and a t–butoxy radical is mentioned. As R301–R337, and a halogen atom of Ra, Rb, Rc, and Rd, a fluorine atom, a chlorine atom, a bromine atom, and iodine atom can be mentioned. The thing of 6–14 carbon numbers which may have a phenyl group, a tolyl group, a methoxyphenyl radical, and a substituent like a naphthyl group as an aryl group of R0, Rc, and Rd is mentioned. The alkoxy group of 1–4 carbon numbers, a halogen atom (a fluorine atom, a chlorine atom, iodine atom), the aryl group of 6–10 carbon numbers, the alkenyl radical of 2–6 carbon numbers, a cyano group, a hydroxy group, a carboxy group, an alkoxy carbonyl group, a nitro group, etc. are mentioned preferably as these substituents.

[0128] As a cyclic hydrocarbon (the oxygen atom and the nitrogen atom may be included in endocyclic [these]) of the ring and monocycle which Rc and Rd combine and form, or many rings, benzene structure, naphthalene structure, cyclohexane structure, norbornene structure, OKISA bicyclo structure, etc. are mentioned.

[0129] The sulfonium expressed with the general formula (AI) used by this invention – (AIII) and an iodonium compound contain that from which the carboxyl group (–COOH) of at least one sort of compounds became an anion (–COO–) as the Xfor anion– among the carboxylic–acid compounds shown by above–mentioned formula (C1) – (C10). The compound expressed with general formula (AIV) used by this invention – (AV) contains the substituent from which the carboxyl group (–COOH) of at least one sort of compounds turned into an ester group (–COO–) as substituents X1 and X2 among the carboxylic–acid compounds shown by above–mentioned formula (C1) – (C10).

[0130] As the shape of a straight chain in R338 of carbon numbers 1–30, the letter of branching, or an annular alkyl group (here, the oxygen atom and the nitrogen atom may be included in the chain of an alkyl group), methyl, ethyl, propyl, butyl, pentyl, hexyl, cyclohexyl, dodecyl, 1–ethoxyethyl, adamantyl, etc. are mentioned. Ethenyl, propenyl, isopropenyl, a cyclohexene, etc. are mentioned as the shape of a straight chain, the letter of branching, or the annular alkenyl radical of carbon numbers 1–20. Acetylene, pro PENIREN, etc. are mentioned as the shape of a straight chain, the letter of branching, or the annular alkynyl group of carbon

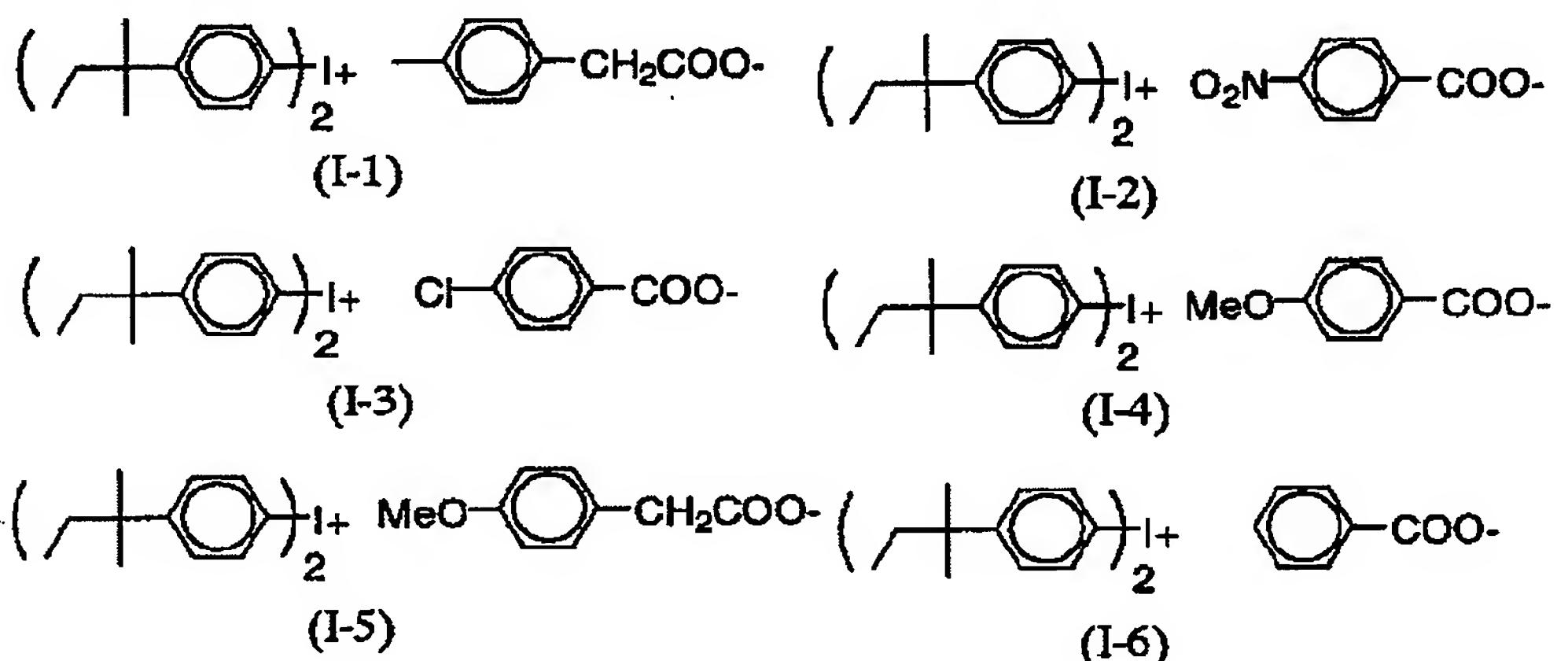
numbers 1–20. As the shape of a straight chain, the letter of branching, or the annular alkoxy group of carbon numbers 1–20, methoxy and ethoxy ** propyloxy, butoxy one, cyclohexyloxy, iso butoxy, dodecyloxy, etc. are mentioned. Phenyl, naphthyl, anthranil, etc. are mentioned as the permutation or the unsubstituted aryl group of carbon numbers 6–20. As a substituent of an aryl group, an alkyl group, a nitro group, a hydroxyl group, an alkoxy group, an acyl group, an alkoxy carbonyl group, and a halogen atom can be mentioned.

[0131] If it considers as the shape of a straight chain in R339 of carbon numbers 1–20, the letter of branching, or an annular alkylene group (here, the oxygen atom and the nitrogen atom may be included in the chain of an alkylene group), methylene, ethylene, a propylene, a butylene, an isobutylene, ethoxyethylene, cyclo hexylene, etc. are mentioned. Vinylene, propene, etc. are mentioned as the shape of a straight chain, the letter of branching, or the annular alkenylene group of carbon numbers 1–20.

[0132] Although an example is shown, this invention is not limited to these.

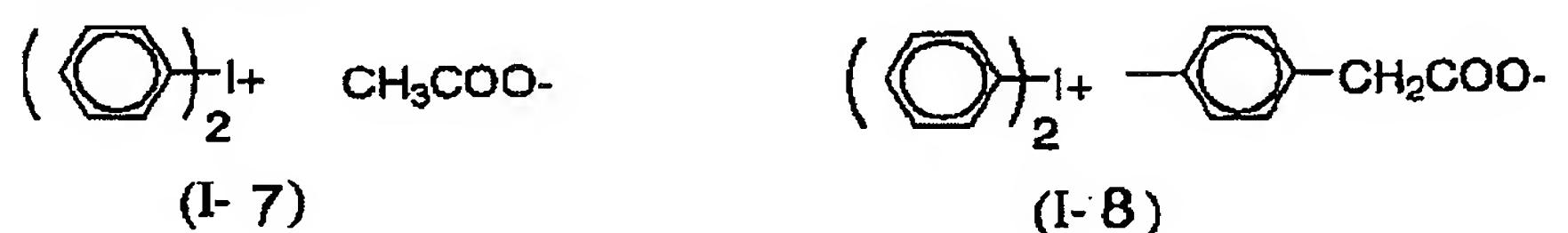
[0133]

[Formula 49]



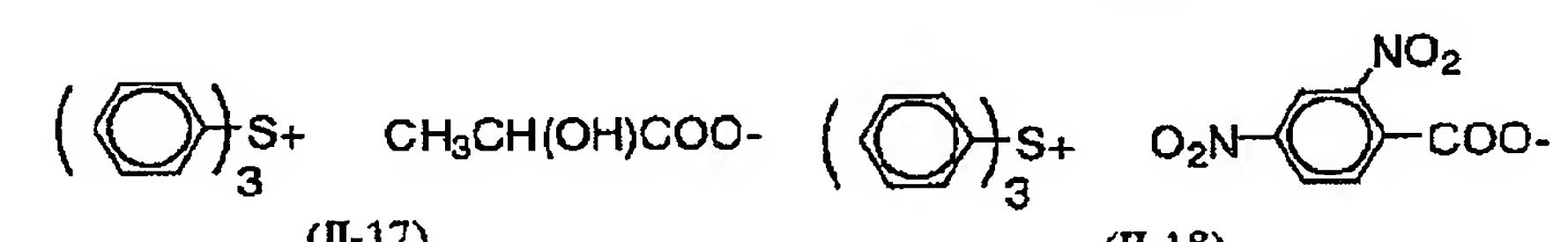
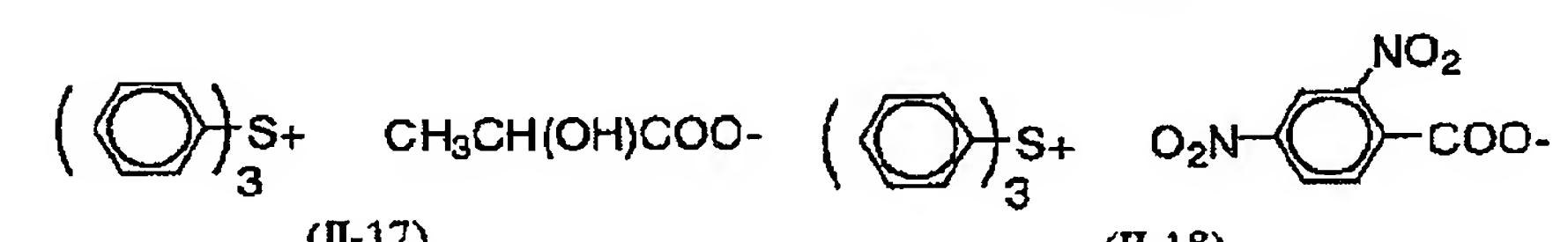
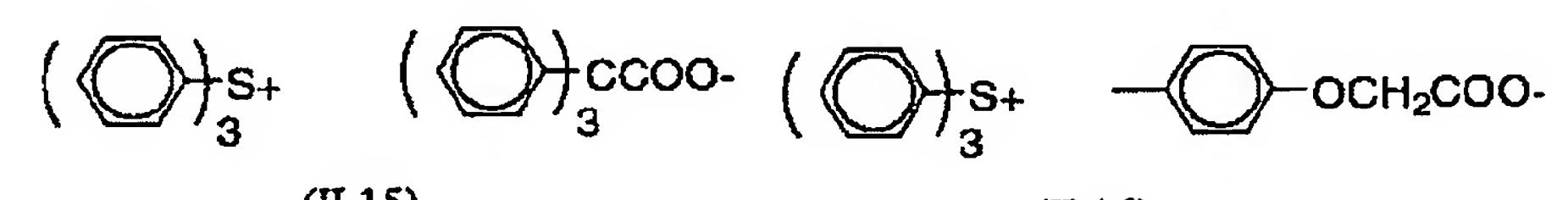
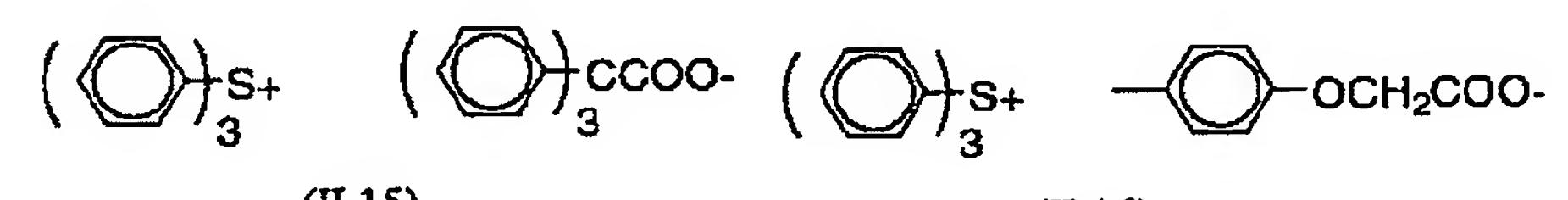
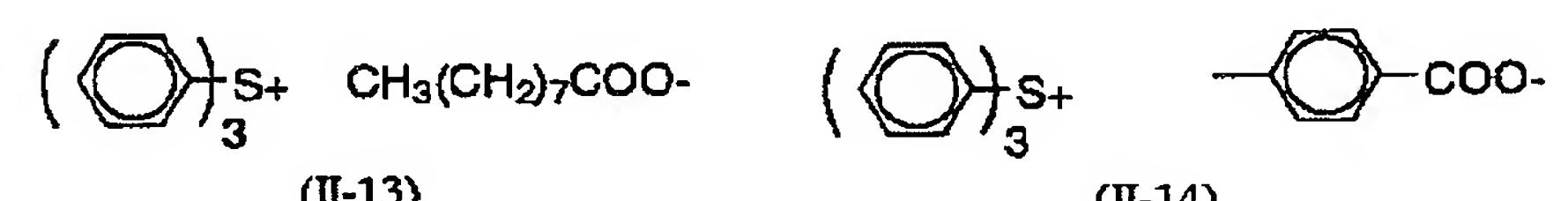
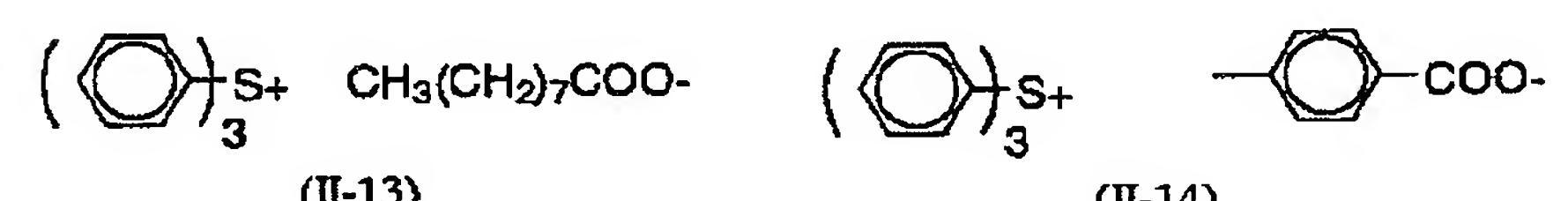
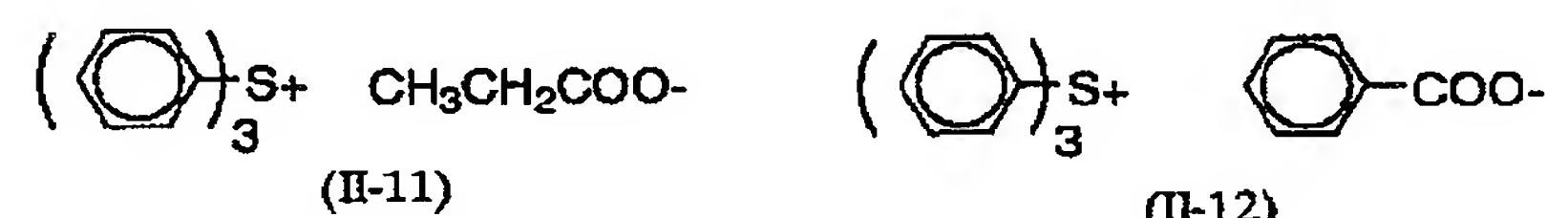
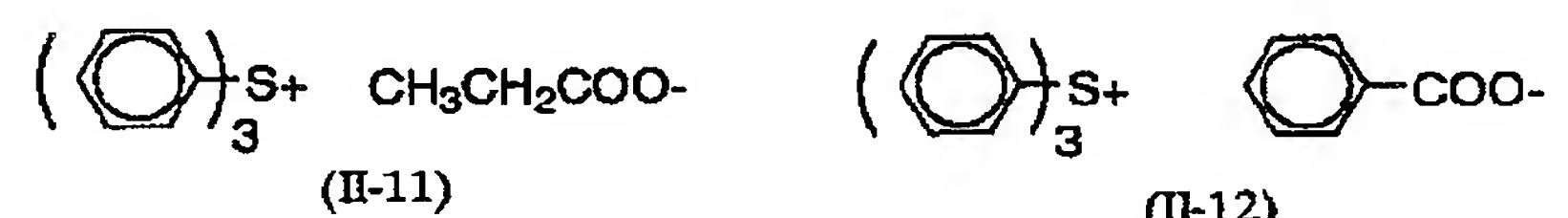
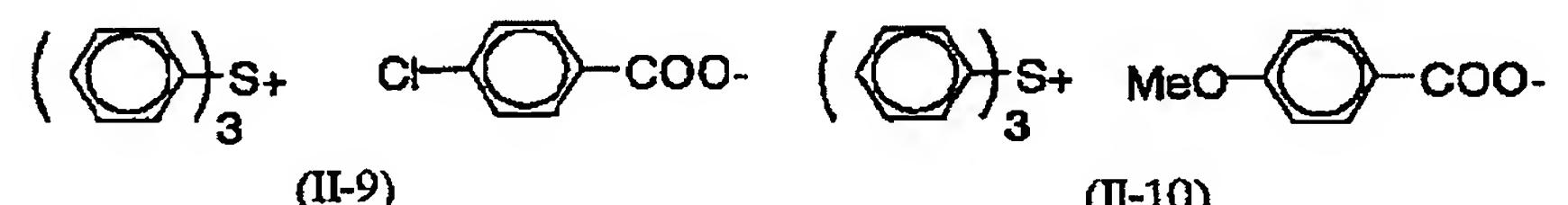
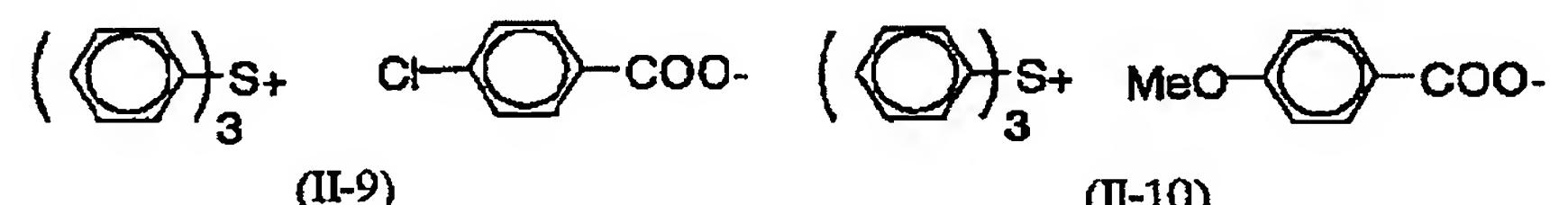
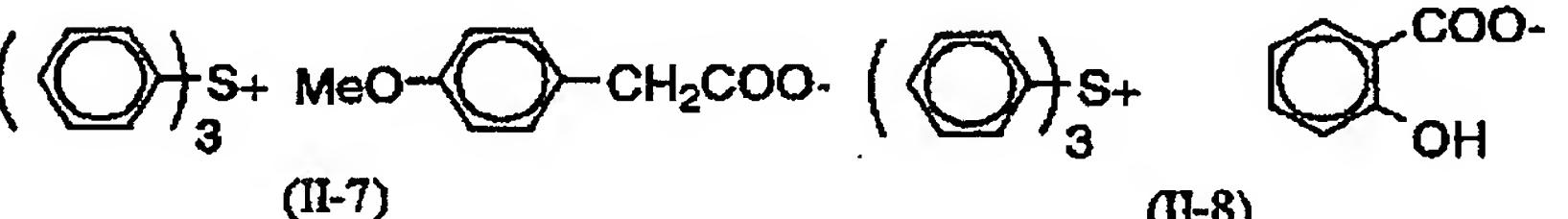
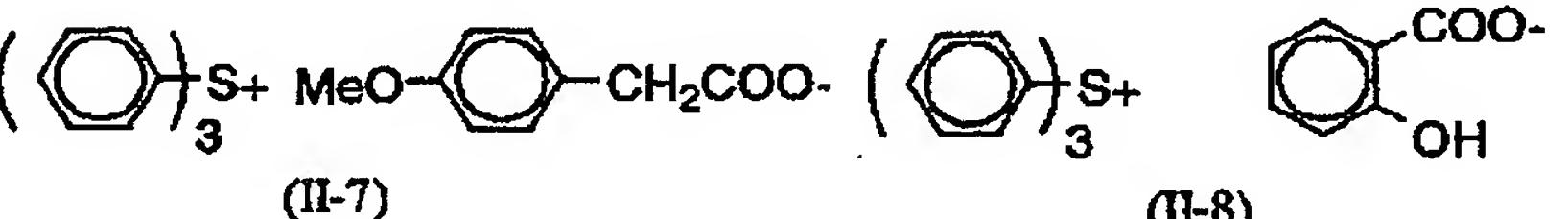
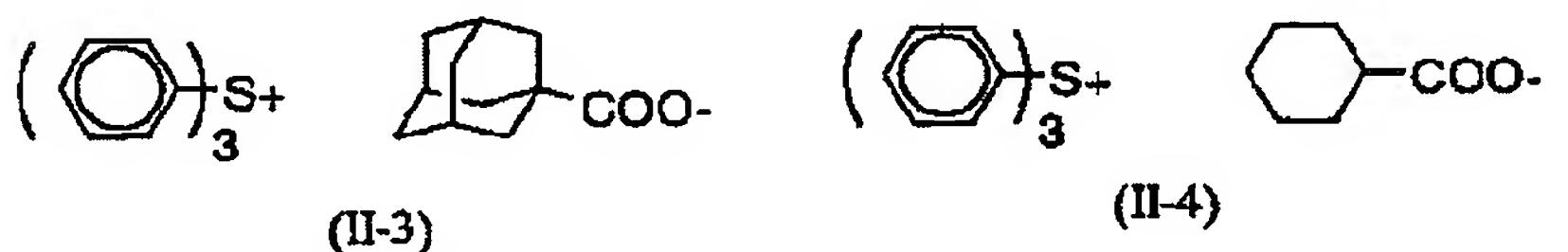
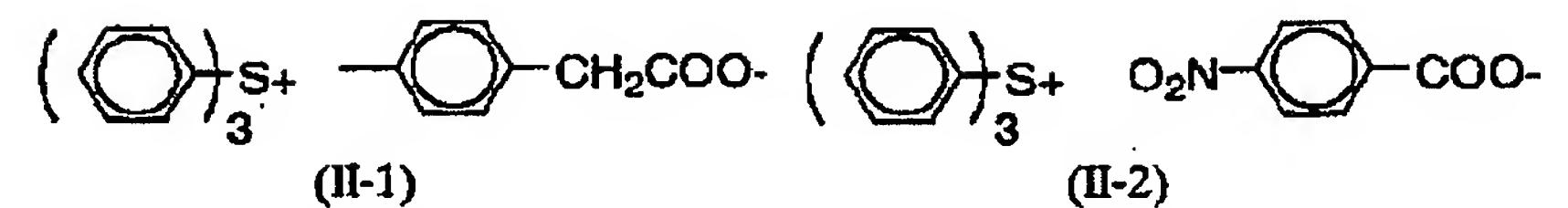
[0134]

〔Formula 50〕



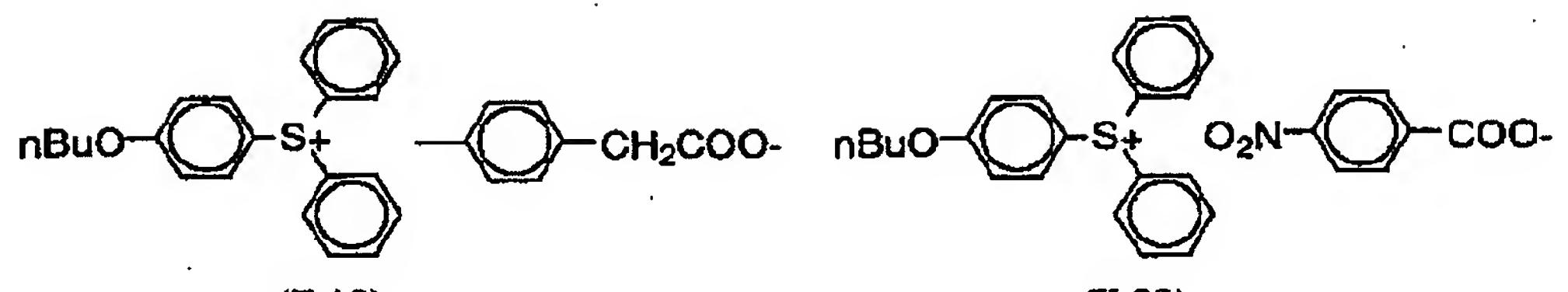
[0135]

[Formula 51]



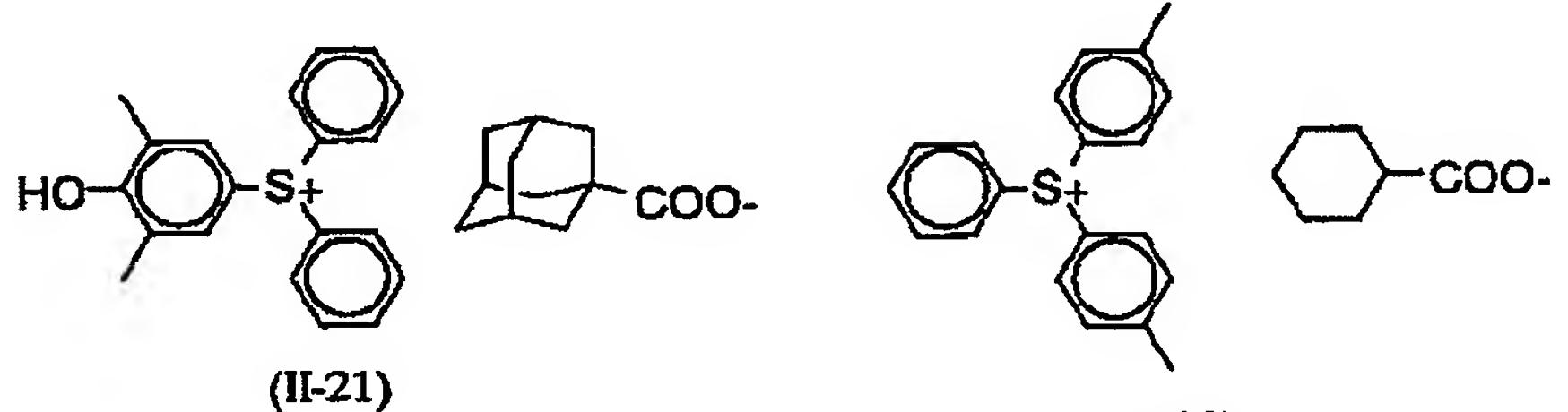
[0136]

[Formula 52]



(II-19)

(II-20)

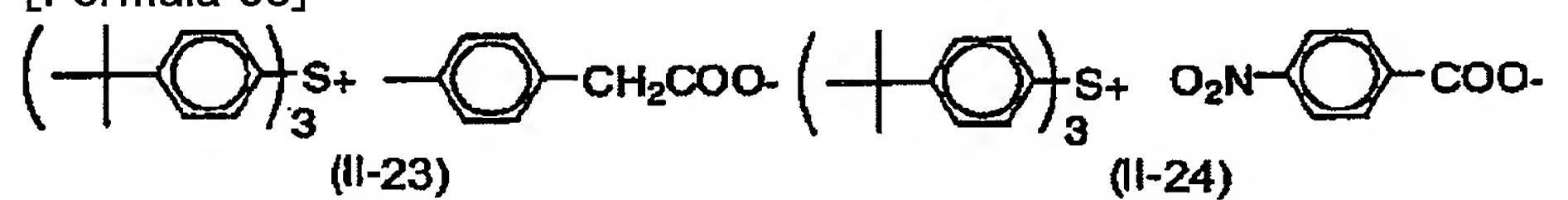


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(II-22)

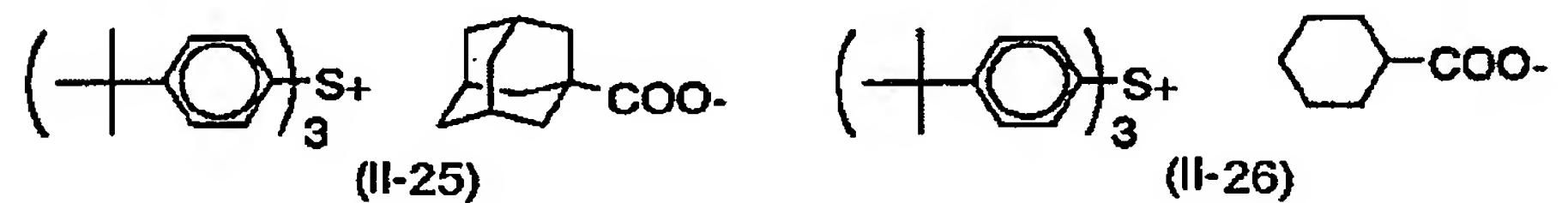
[0137]

[Formula 53]



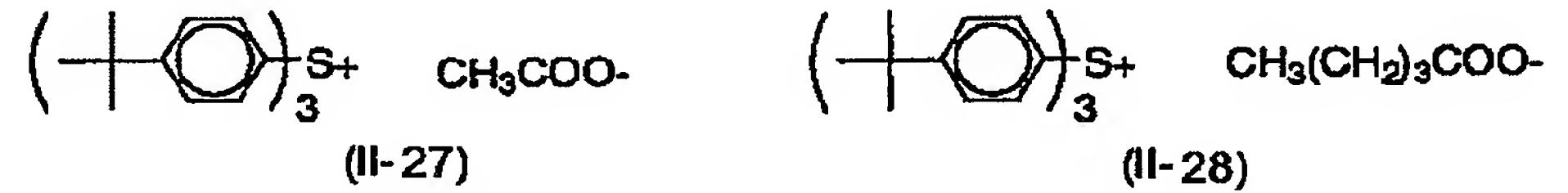
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(II-26)

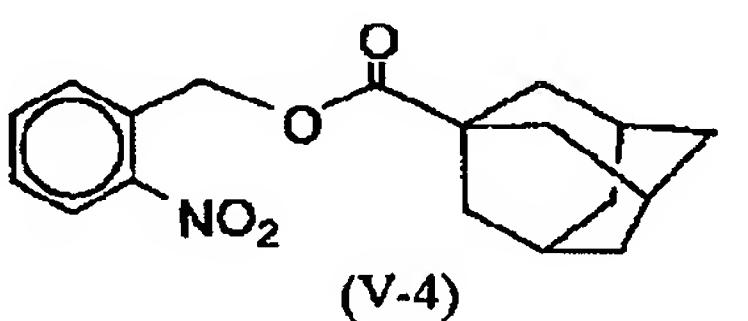
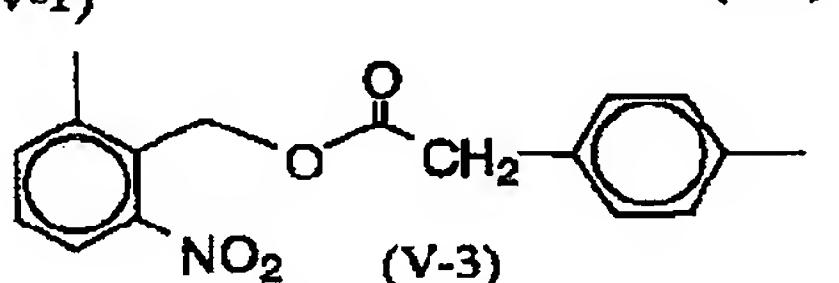
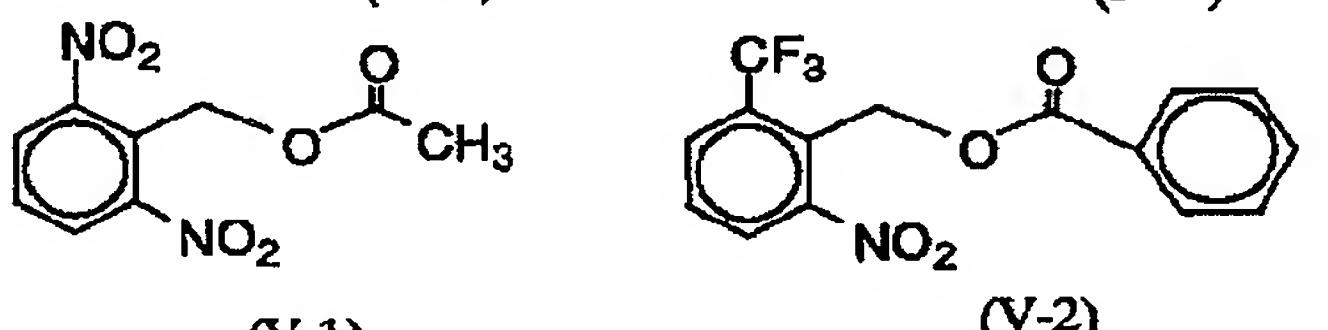
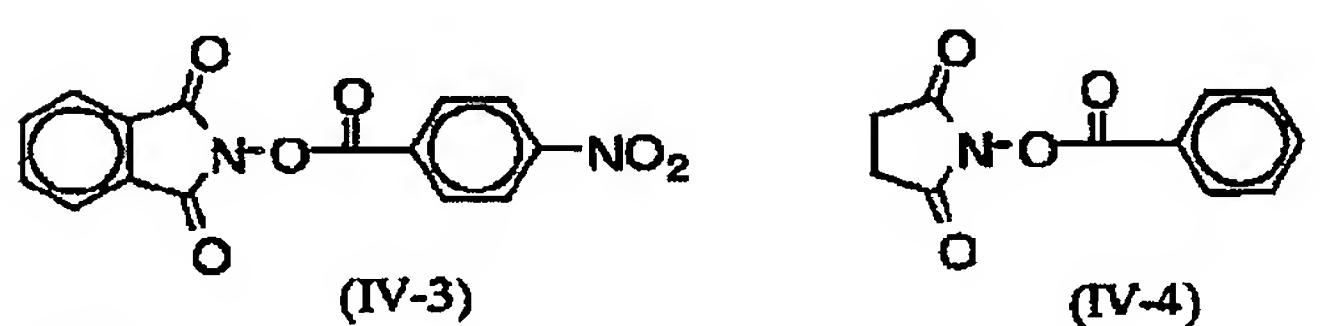
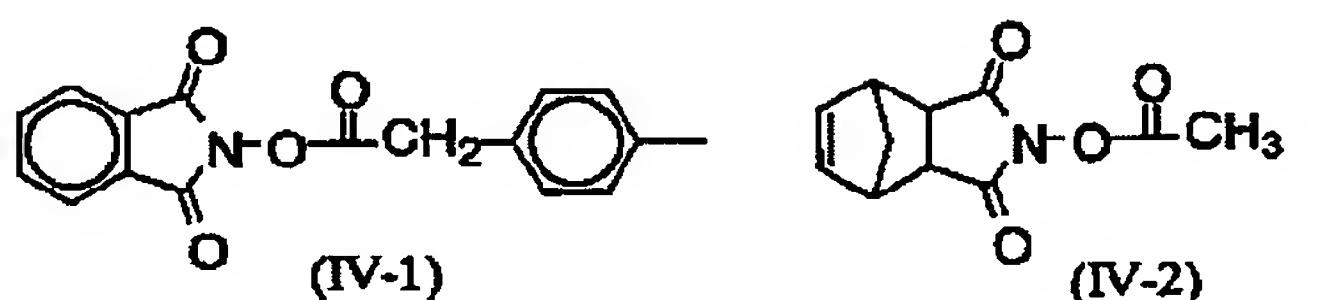
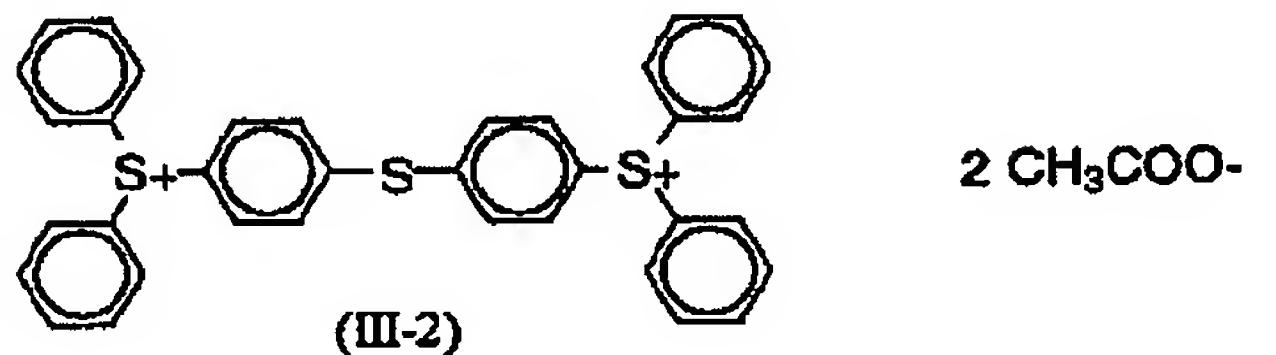
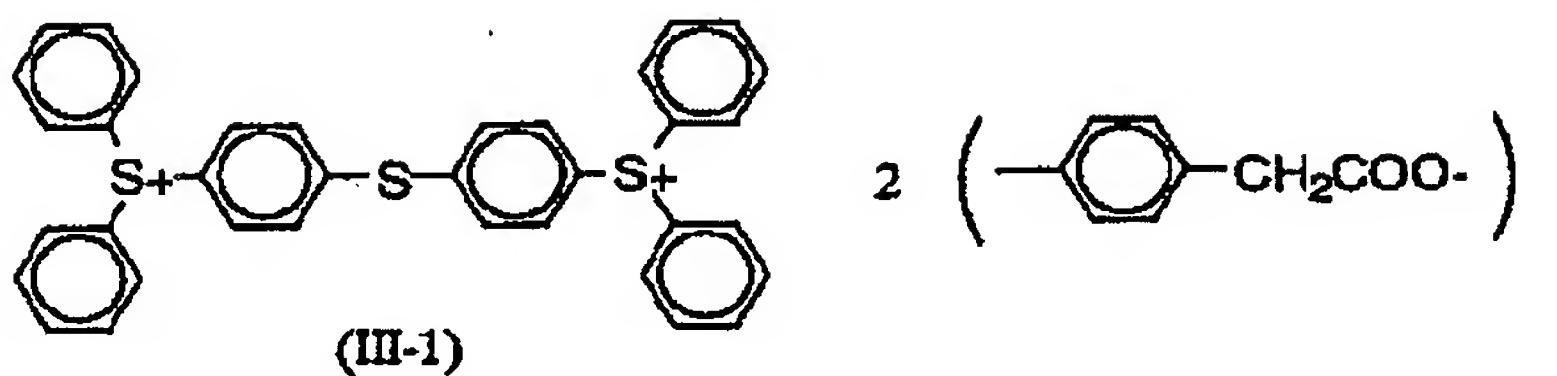


(II-27)

(II-28)

[0138]

[Formula 54]



[0139] The compound expressed with a general formula (AI), a general formula (AII), and a general formula (AIII) An approach given in a U.S. Pat. No. 3,734,928 specification, Macromolecules, vol.10, 1307 (1977), Journal of Organic Chemistry, vol.55, 4222 (1990), J.Radiat.Curing, vol.5(1), and 2 (1978) It is compoundable by exchanging a counter anion further using the approach of a publication etc. The compound expressed with a general formula (AIV) and a general formula (AV) makes an N-hydroxy imide compound and carboxylic-acid chloride react on basic conditions, or is obtained by making nitrobenzyl alcohol and carboxylic-acid chloride react under a basic condition.

[0140] In this invention, the contrast of concentration distribution of the strong acid generated by the exposure of an activity beam of light, an activity beam of light [/ near the interface (the amount exposure region of low energy) of the exposure section / non-irradiating section of a radiation], or a radiation can be

raised by using together a component (A1) and a component (A2).

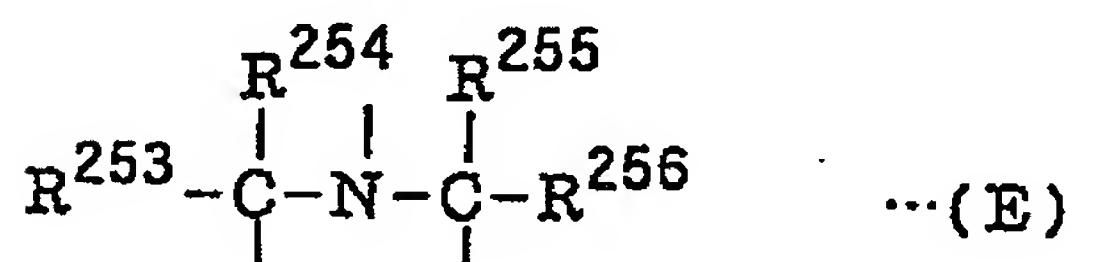
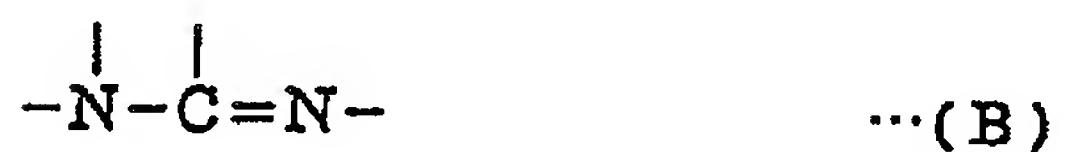
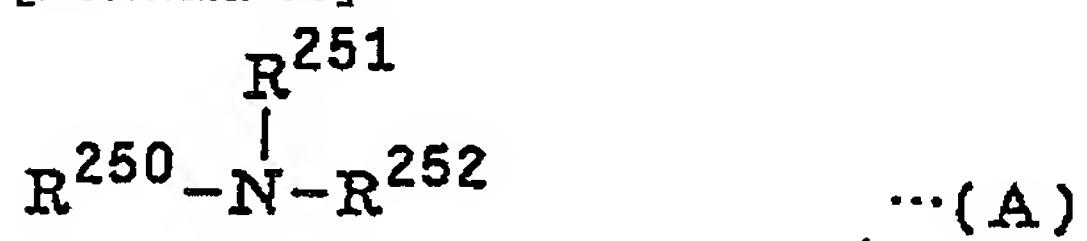
[0141] (A1) the weight ratio of the addition of a component and a component (A2) -- usually -- 100 / 100 -- 100/0 -- desirable -- 100 / 100 -- 100/10 -- it is 100 / 50 -- 100/20 especially preferably. (A1) the total quantity of a component and a component (A2) -- constituent total solids -- receiving -- usually -- it is 1 -- 10% of the weight of the range more preferably 0.75 to 15% of the weight 0.5 to 20% of the weight. (A1) Two or more components and (A2) components may carry out seed content respectively.

[0142] [3] Organic base nature compound (D component)

To the constituent of this invention, after the exposure of an activity beam of light or a radiation, it is desirable to add an organic base nature compound in order to prevent the engine--performance fluctuation (T-top configuration formation of a pattern, sensibility fluctuation, pattern line breadth fluctuation, etc.) by the passage of time to heat--treatment, the engine--performance fluctuation by the passage of time after spreading, and superfluous diffusion (degradation of resolution) of the acid at the time of heat--treatment after the exposure of an activity beam of light or a radiation further. As an organic base nature compound, it is the organic base compound which contains basic nitrogen, for example, and four or more compounds are preferably used with the electric dissociation exponent value of a conjugate acid. Specifically, the structure of following type (A) -- (E) can be mentioned.

[0143]

[Formula 55]



[0144] Here, it is R250 and R251. And R252 It may be the same, or you may differ and the permutation of a hydrogen atom, the alkyl group of 1-6 carbon numbers, the amino alkyl group of 1-6 carbon numbers, the hydroxyalkyl radical of 1-6 carbon numbers, or 6-20 carbon numbers or an unsubstituted aryl group is expressed, it may join together mutually and R251 and R252 may form a ring here. R253, R254, and R255 And R256 It may be the same, or you may differ and the alkyl group of 1-6 carbon numbers is expressed. Furthermore, a desirable compound is a nitrogen-containing basicity compound which has two or more

nitrogen atoms of different chemical environment in a monad, and is a compound which has especially a compound or alkylamino radical including both ring structures containing the amino group and nitrogen atom which are not permuted [a permutation or] preferably.

[0145] As a desirable example, the aminopyridine which is not permuted [the guanidine which is not permuted / a permutation or / a permutation, or], The amino pyrrolidine which is not permuted [the amino alkyl pyridine which is not permuted / a permutation or / a permutation, or], The pyrazole which is not permuted [the indazole which is not permuted / a permutation or /, an imidazole, a permutation, or], The pyrimidine which is not permuted [the pyrazine which is not permuted / a permutation or /, a permutation, or], The amino alkyl morpholine which is not permuted [the amino morpholine which is not permuted / the piperazine which is not permuted / the pyrazoline which is not permuted / the imidazoline which is not permuted / the piperazine which is not permuted / a permutation or /, a permutation, or /] is mentioned. Desirable substituents are the amino group, an amino alkyl group, an alkylamino radical, an amino aryl group, an arylamino radical, an alkyl group, an alkoxy group, an acyl group, an acyloxy radical, an aryl group, an aryloxy group, a nitro group, a hydroxyl group, and a cyano group.

[0146] As a desirable compound, especially Guanidine, 1, and 1-dimethyl guanidine, 1, 1, 3, 3, - tetramethyl guanidine, an imidazole, 2-methylimidazole, 4-methyl imidazole, N-methyl imidazole, 2-phenylimidazole, 4, 5-diphenyl imidazole, 2 and 4, 5-triphenyl imidazole, 2-aminopyridine, 3-aminopyridine, 4-aminopyridine, 2-dimethylamino pyridine, 4-dimethylaminopyridine, 2-diethylamino pyridine, 2-(aminomethyl) pyridine, 2-amino-3-methylpyridine, 2-amino-4-methylpyridine, 2-amino-5-methylpyridine, 2-amino-6-methylpyridine, 3-aminoethyl pyridine, 4-aminoethyl pyridine, [0147] 3-amino pyrrolidine, a piperazine, N-(2-aminoethyl) piperazine, N-(2-aminoethyl) piperidine, 4-amino - 2, 2, 6, and 6-tetramethylpiperidine, 4-piperidino piperidine, a 2-imino piperidine, 1-(2-aminoethyl) pyrrolidine, A pyrazole, 3-amino-5-methyl pyrazole, 5 - Amino-3-methyl-1-p-tolyl pyrazole, Pyrazine, 2-(aminomethyl)-5-methyl pyrazine, a pyrimidine, Although 2, 4-diamino pyrimidine, 4, 6-dihydroxy pyrimidine, 2-pyrazoline, 3-pyrazoline, N-amino morpholine, N-(2-aminoethyl) morpholine, etc. are mentioned, it is not limited to this. These nitrogen-containing basicity compounds are independent, or are used together two or more sorts.

[0148] As for the operating rate in the constituent of an acid generator and an organic base nature compound, it is desirable that it is a (acid generator) / (organic base nature compound) (mole ratio) =2.5-300. This mole ratio may serve as low sensibility less than by 2.5, resolving power may decline, and if 300 is exceeded, *** of a resist pattern may become large by the passage of time to exposure afterbaking processing, and resolving power may also decline. a (acid generator) -- / (organic base nature compound) (mole ratio) -- desirable -- 5.0-200 -- it is 7.0-150 still more preferably.

[0149] [4] As for the constituent of surfactant this invention, it is desirable to contain a surfactant especially a fluorine system, and/or a silicon system surfactant. That is, it is desirable to contain either of the surfactants containing both a fluorochemical surfactant, a silicon system surfactant and a fluorine atom, and a silicon atom or two sorts or more in the constituent of this invention. Addition of these fluorines system and/or a silicon system surfactant has effectiveness in control of a development defect, and improvement in spreading nature.

[0150] As these surfactants, for example, JP,62-36663,A, JP,61-226746,A, JP,61-226745,A, JP,62-170950,A, JP,63-34540,A, JP,7-230165,A, JP,8-62834,A, JP,9-54432,A, JP,9-5988,A, a U.S. Pat. No. 5405720 number, a U.S. Pat. No. 5360692 number, A U.S. Pat. No. 5529881 number, a U.S. Pat. No. 5296330 number, a U.S. Pat. No. 5436098 number, A U.S. Pat. No. 5576143 number, a U.S. Pat. No. 5296143 number, a U.S. Pat. No. 5294511 number, and a surfactant given in a U.S. Pat. No. 5824451 number can be mentioned, and the surfactant of the following marketing can also be used as it is. As a surfactant of such marketing, for example, EFUTOPPU EF301, EF303, and EF352 (new Akita formation Make), Fluorad 430 and FC 431 (Sumitomo 3M make), the megger fucks F171, F173, F176, F189, and R08 (Dainippon Ink make), A fluorochemical surfactant or silicon system surfactants, such as the Asahi guard AG710, Sir chlorofluorcarbon S-382, SCs 101, 102, 103, 104, 105, and 106 (Asahi Glass Co., Ltd. make), and Troysol S-366 (made in Troy Chemical), can be mentioned. Moreover, polysiloxane polymer KP-341 (Shin-Etsu Chemical Co., Ltd. make) can be used as a silicon system surfactant.

[0151] The loadings of a surfactant are usually 0.01 % of the weight – 1 % of the weight preferably on the basis of the solid content in the constituent of this invention 0.001 % of the weight to 2% of the weight. You may add independently and these surfactants can also be added in some combination.

[0152] [5] Solvent (C component)

The constituent of this invention is melted to the solvent which dissolves each above-mentioned component, and is applied on a base material. As a solvent used here, ethylene dichloride, a cyclohexanone, Cyclopentanone, 2-heptanone, gamma-butyrolactone, a methyl ethyl ketone, Ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, 2-methoxy ethyl acetate, ethylene glycol monoethyl ether acetate, Propylene glycol monomethyl ether, the propylene glycol monoethyl ether, Propylene-glycol-monomethyl-ether acetate, toluene, ethyl acetate, Methyl lactate, ethyl lactate, methoxy methyl propionate, ethoxy ethyl propionate, methyl pyruvate, pyruvic-acid ethyl, pyruvic-acid propyl, N.N-dimethylformamide, dimethyl sulfoxide, N-methyl pyrrolidone, a tetrahydrofuran, etc. are desirable, and independent in these solvents -- or it is mixed and used. In this invention, it is desirable to use as a solvent the partially aromatic solvent which mixed propylene glycol monoalkyl ether acetate, such as propylene-glycol-monomethyl-ether acetate, and lactic-acid alkyls, such as propylene glycol monoalkyl ether, such as propylene glycol monomethyl ether and the propylene glycol monoethyl ether, or methyl lactate, and ethyl lactate. As for the solid content concentration at the time of dissolving each above-mentioned component in a solvent, it is desirable to consider as 3 – 15 % of the weight, and it is more desirable to consider as 5 – 10 % of the weight.

[0153] In manufacture of a precision integrated circuit device etc., on substrates (example: transparency substrates, such as silicon / diacid-ized silicon leather **, a glass substrate, and an ITO substrate etc.), the constituent of this invention can be applied, it can irradiate by the ability using an activity beam of light or radiation drawing equipment next, and the pattern formation process to a resist film top can form a good resist pattern heating, development, a rinse, and by drying.

[0154] As a developer of the constituent of this invention, a sodium hydroxide, a potassium hydroxide, Inorganic alkali, such as a sodium carbonate, a sodium silicate, a meta-sodium silicate, and aqueous ammonia Primary amines, such as ethylamine and n propylamine, diethylamine, Tertiary amines, such as secondary amines, such as G n butylamine, triethylamine, and methyl diethylamine Alcoholic amines, such as

dimethylethanolamine and a TORIETA no amine, The water solution of alkali, such as annular amines, such as quarternary ammonium salt, such as tetramethylammonium hydroxide, tetraethylammonium hydroxide, and a choline, a pyrrole, and a piperidine, can be used. Furthermore, surfactants, such as alcohols, such as isopropyl alcohol, and the Nonion system, can also be used for the water solution of the above-mentioned alkali, carrying out suitable amount addition. the inside of these developers -- desirable -- quaternary ammonium salt -- they are tetramethylammonium hydroxide and a choline still more preferably.

[0155]

[Example] Hereafter, although an example explains this invention to a detail further, thereby, the contents of this invention are not limited.

[0156] The example 1 (composition of an organic fluorine polymer (F-1)) of <composition of organic fluorine polymer> composition

3-(5-bicyclo [2.2.1] heptene-2-IRU)- 1, 1, and 1-trifluoro-2-(trifluoromethyl)-2-propane-2-all 27.5g and acrylonitrile 5.4g -- 4-(2-hydroxy hexafluoro isopropyl) styrene 23.8g is added to THF100ml, and azo system polymerization initiator V-65 (Wako Pure Chem industrial company make) 1.24g was added, and it was made to react under 1-hour stirring at the place warmed at 65 degrees C. there -- 3-(5-bicyclo [2.2.1] heptene-2-IRU)- 1, 1, and 1-trifluoro-2-(trifluoromethyl)-2-propane-2-all 27.5g and acrylonitrile 5.4g -- 4-(2-hydroxy hexafluoro isopropyl) styrene What melted 41.4g and azo system polymerization initiator V-65 (Wako Pure Chem industrial company make) 2.48g to THF100ml was dropped over 4 hours, and it was made to react under 4 more hour stirring. After adding hexane 500ml to reaction mixture and settling a polymer, the upper layer was removed in the decantation. The ***** polymer which remained was melted to acetone 50ml, by adding hexane 1L again, judgment processing of the polymer was carried out and the unreacted monomer and the oligomer component were removed. When the determination of molecular weight was performed for the obtained polymer in GPC, weight average molecular weight was 10200 and degree of dispersion was 1.5. After dissolving obtained polymer 17.5g in THF, had 2 carbonic-acid JI t-butyl 10.4g in addition and a pan, had a dimethylamino pyridine in the catalyst, it was made to have been and to react, and the organic fluorine polymer (F-1) was obtained. When the determination of molecular weight was performed for the obtained polymer in GPC, weight average molecular weight was 10200 and degree of dispersion was 1.4.

[0157] The synthetic example 2 (composition of an organic fluorine polymer (F-2))

3-(5-bicyclo [2.2.1] heptene-2-IRU)- 1, 1, and 1-trifluoro-2-(trifluoromethyl)-2-propane-2-all 10.8g -- After heating azobisisobutironitoriru1.24g and TEMPO1.41g at addition and 80 degrees C at the place which added methacrylonitrilesg [3.4] and 3 and 5-bis(2-hydroxy hexafluoro isopropyl) styrene 8.7g to toluene 200ml, it was made to react under 18-hour stirring. After adding hexane 500ml to reaction mixture and settling a polymer, the upper layer was removed in the decantation. When the determination of molecular weight was performed for the obtained organic fluorine polymer (F-6) in GPC, weight average molecular weight was 19000 and degree of dispersion was 1.5. Similarly, the organic fluorine polymer of a publication was obtained to the following table 1.

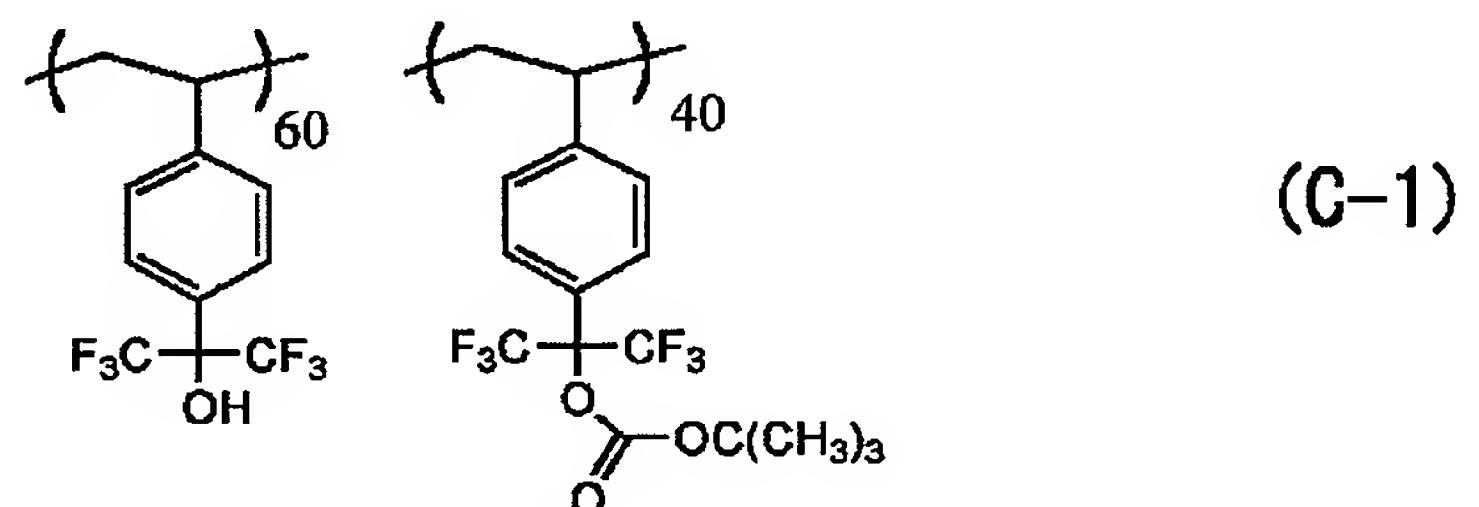
[0158] The synthetic example 3 (composition of the organic fluorine polymer (C-1) of the example of a comparison)

Azo system polymerization initiator V-65 (Wako Pure Chem industrial company make) 1.24g was added to

the place which melted 4-(2-hydroxy hexafluoro isopropyl) styrene 16.6g and 4-(2-hydroxy hexafluoro isopropyl) styrene 15.0g protected by t-butoxycarbonyl to THF80ml, and it was made to react at 65 degrees C as it is to it for 16 hours. Hexane 500ml was added to the place which diluted reaction mixture with the acetone, and the polymer was settled at it. The obtained polymer was dried under reduced pressure and the organic fluorine polymer (C-1) of the example of a comparison was obtained. When the determination of molecular weight was performed for the obtained polymer in GPC, weight average molecular weight was 21500 and degree of dispersion was 2.2. The structure of an organic fluorine polymer (C-1) is as follows.

[0159]

[Formula 56]



[0160]

[Table 1]

表1

有機フッ素 ポリマー	モル組成比*	重量平均 分子量	分子量 分散度
(F-1)	5/20/50/25	10200	1.4
(F-2)	30/50/20	19000	1.5
(F-4)	30/40/30	8900	1.5
(F-5)	20/20/40/20	17000	1.5
比較例 (C-1)	60/40	21500	2.2

* 各繰り返し構造単位の左からの順番に対応

[0161] Example 1 of <composition of acid generator> composition (composition of triphenylsulfonium NONAFURORO butane sulfonate (VII-4))

Triphenylsulfonium iodide 20g was dissolved in methanol 500ml, 12.5g of silver oxides was added to this, and it stirred at the room temperature for 4 hours. After filtering reaction mixture and removing a silver compound, NONAFUROROBUTAN sulfo nick acid 14.9g was added to this solution, and this solution was condensed. After adding diisopropyl ether 300ml to the obtained oily matter and fully stirring, the actuation except diisopropyl ether was repeated twice by decant. When reduced pressure drying of the obtained oily matter was carried out, 18g of specified substance was obtained.

[0162] Synthetic example 2 (composition of triphenylsulfonium-4-dodecylbenzene sulfonate (PAG 4-1))

Triphenylsulfonium iodide 10g was dissolved in methanol 500ml, 4.44g of silver oxides was added to this, and it stirred at the room temperature for 4 hours. After filtering reaction mixture and removing a silver compound, 4-dodecylbenzene sulfo nick acid 4.67g was added to this solution, and this solution was condensed. After adding diisopropyl ether 300ml to the obtained oily matter and fully stirring, the actuation except diisopropyl ether was repeated twice by decant. When reduced pressure drying of the obtained oily matter was carried out, 6g of specified substance was obtained.

[0163] Synthetic example 3 (composition of triphenylsulfonium nona FURORO pentanoate (II-4f))

Triphenylsulfonium iodide 20g was dissolved in methanol 500ml, 12.5g of silver oxides was added to this, and four intervals of clear weather were agitated at the room temperature. After filtering reaction mixture and removing a silver compound, nona FURORO pentanoic acid 14.9g was added to this solution, and this solution was condensed. After adding diisopropyl ether 300ml to the obtained oily matter and fully agitating, the actuation except G SOPUROPIBIRUETERU was repeated twice by decant. When reduced pressure drying of the obtained oily matter was carried out, 18g of specified substance was obtained.

[0164] The organic fluorine polymer shown in examples 1–4 and the [example [of a comparison] 1] following table 2: The polymer solution which dissolved 100 ppm and organic base nature compound:0.0012g in 19.6g of solvents to 1.2g, acid generator:0.030g, and a surfactant:polymer solution was filtered with the 0.1-micrometer Teflon (trademark) filter, and positive-resist liquid was prepared.

[0165]

[Table 2]

表2

	有機フッ素 ポリマー	酸発生剤 (重量比)	溶剤 (重量比)	有機塩基性 化合物	界面 活性剤
実施例 1	(F-1)	(VII-4)/(II-4f) (60/40)	S-2	N-1	W-1
実施例 2	(F-2)	(VII-4)/(II-4f) (60/40)	S-2/S-1 (80/20)	N-1	W-1
実施例 3	(F-4)	(VII-24)/(II-1f) (50/50)	S-2	N-1	W-1
実施例 4	(F-5)	(VII-36)/(PAG4-1) (50/50)	S-2/S-3 (80/20)	N-2	W-2
比較例 1	(C-1)	(VII-4)	S-2	N-1	W-1

[0166] The contents of the notation in Table 2 are as follows.

N-1: A hexamethylenetetramine N-2:1, 5-diazabicyclo [4.3.0]–5–nonene W-1 : megger fuck F176 (Dainippon Ink & Chemicals, Inc. make) (fluorine system)

W-2: Megger fuck R08 (Dainippon Ink & Chemicals, Inc. make) (a fluorine and silicon system)

S-1: Methyl lactate S-2:propylene–glycol–monomethyl–ether acetate S-3 : propylene glycol monomethyl ether [0167] The positive-resist liquid prepared as mentioned above was applied to homogeneity on the silicon wafer which applied the antireflection film (DUV42–6 BrewerScience.Inc. make) using the spin coater, stoving was performed for 120-degree-C 60 seconds, and the positive-resist film of 0.1 micrometers of thickness was formed. Pattern exposure was carried out using the mask for Rhine and tooth spaces (Rhine width of face of 150nm, Rhine/tooth space = 1:1) using the KrF micro stepper, and it heated on the hot plate for 110-degree-C 90 seconds immediately after exposure to this resist film. Negatives were developed for 30 seconds at 23 degrees C with the tetramethylammonium hydronium oxide water solution 2.38 more%, and it dried, after carrying out a rinse with purity for 30 seconds. Thus, the following approach estimated the resist engine performance for the pattern on the obtained silicon wafer.

[0168] The [Rhine edge roughness] About the range of edge 5micrometer of the longitudinal direction of the Rhine pattern, the distance from the datum line which should have an edge was measured 50 point by length measurement SEM (Hitachi Make S-8840), it asked for standard deviation, and 3sigma was computed. It is

shown that a value is small that it is such good engine performance.

[0169] [Development defective evaluation trial] About the resist pattern obtained as mentioned above, the number of development defects was measured by the KLA-2112 set by the KEERUE ten call company, and the acquired primary data value was made into the measurement result. The performance-evaluation result was shown in Table 3.

[0170]

[Table 3]

表3

	ラインエッジ ラフネス(nm)	現像欠陥数
実施例 1	10.4	28
実施例 2	10.3	23
実施例 3	11.0	27
実施例 4	10.8	26
比較例 1	14.0	64

[0171] From the result of Table 3, the constituent of this invention is understood that the Rhine edge roughness and the development engine performance are good.

[0172]

[Effect of the Invention] By this invention, the positive-resist constituent with which the Rhine edge roughness and the development defective engine performance have been improved can be offered.

[Translation done.]